A Study of Certain β-nitrostyrenes Functionally Capable
of Independent Anionic and Cationic Initiation

By

JAMES WESLEY SCHWIETERT

## ACKNOWLEDGMENTS

The author wishes to express his deep appreciation and gratitude for the encouragement and guidance provided by his research director, Prof. George B. Butler. Suggestions and comments by other members of his supervisory committee as well as Dr. Thieo Hogen-Esch were also very helpful.

The author's wife, Rose, has been of inestimable value toward the completion of this work. Her continued love and devotion despite months of neglect is very gratefully acknowledged. Her patience, moral support and typing of this dissertation were also appreciated .

Fellow students in this laboratory have made the author's work atmosphere a very pleasant one and their friendship and advice are appreciated. Many helpful discussions with Dr. Kiyo Fujimori and Dr. Bruno Zeegers have been particularly rewarding.

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A STUDY OF CERTAIN BETA-NITROSTYRENES FUNCTIONALLY CAPABLE
OF INDEPENDENT ANIONIC AND CATIONIC INITIATION

By

James Wesley Schwietert

June, 1971

Chairman: G. B. Butler
Major Department: Chemistry

The purpose of this work was to synthesize and polymerize a
set of ideal cross-linking monomers which could be selectively polymer-
ized through one vinylic moeity to a linear soluble polymer followed
by selective cross-linking via another pendant vinylic moeity. A study
was also initiated to determine the effect of various substituents on
the anionic polymerizations of various beta-nitrostyrenes. A study of
ortho-substituted beta-nitrostyrenes, which had been previously reported
to be resistant to anionic polymerization, was also initiated.

The three isomers of (2-vinyloxy)ethoxy-beta-nitrostyrene have
been synthesized and found to selectively polymerize anionically through
the nitrovinyl moeity upon reaction with an alkoxide. They have also
been found to selectively polymerize cationically through the vinyloxy
group upon reaction with a Lewis acid.

A kinetic study of the anionic polymerization of beta-styrenes
has been conducted using a gravimetric method and the relative rates of
propagation unexpectedly found to correlate well with Brown's sigma$^{+}$
values. The rates of initiation of two monomers with sodium ethoxide
have been found to be rapid. The rate of chain transfer in ethanol has

been studied qualitatively using gel permeation chromatography to obtain molecular weight distribution curves. The low values of the ratios of weight-average molecular weight to number-average molecular weight indicate little chain transfer in the protic solvent.

All ortho-substituted beta-nitrostyrenes except the ortho-fluoro compound have been found to be resistant to anionic polymerization. This phenomenon has been unambiguously shown to be the result of inhibition of propagation and not initiation.

# CHAPTER I

## INTRODUCTION

### Background

A.  General Background

β-nitrostyrene was probably first polymerized anionically by Priebs[1] who was studying the effect of alkalies on the compound. He reported obtaining amorphous products. The polymerizations of some β-nitrostyrenes have been studied to some extent[2,3,4] but the mechanism has not been examined in detail nor have many properties of the polymers been studied. This fact is primarily due to the poor solubility of the polymers in common organic solvents.

The solubility problem not only prevents spectroscopic analysis of the polymerization reaction but prohibits molecular weight determination as well as determination of other properties of the polymers. In earlier work, Butler[5] succeeded in determining the molecular weights of some samples of poly-β-nitrostyrene by an ebullioscopic method in butanone. He also made the interesting observation that poly-β-nitrostyrene apparently underwent depolymerization after being heated in dimethylformamide as evidenced by lower molecular weights. Other substituted poly-β-nitrostyrenes were reported insoluble in all solvents tried.[6,7]

The apparent ease with which β-nitrostyrene anionically polymerizes is principally due to the strong electron withdrawing

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capability of the nitro group, both by inductive and resonance effects. This makes the vinylic double-bond, in general, electron deficient and the $\alpha$-carbon, in particular, vulnerable to nucleophilic attack. For the same reasons the compound appears to be resistant to cationic and free radical polymerizations.

On the other hand, the electron-rich vinyl ethers have been found to be very susceptible to electrophilic attack by Lewis or Bronsted acids. This attack may lead to hydrolysis of the ether in the presence of water[8] or polymerization under anhydrous conditions.[9,10,11] At the same time, vinyl ethers have been found to be quite resistant to nucleophilic attack.

B.  Synthesis and Chemistry of the (2-vinyloxy)ethoxy-β-nitrostyrenes

This wide variation in reactivity between the two types of vinyl groups makes them ideal functional groups for two-stage polymerizations. It was with this goal in mind that Nash[12] attempted to synthesize ortho-, meta-, and para-(2-vinyloxy)ethoxy-β-nitrostyrene.
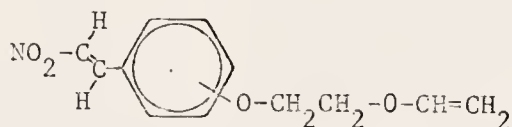


The method of synthesis requires first reacting the potassium salt of the corresponding hydroxybenzaldehyde with β-chloroethyl vinyl ether (Williamson synthesis) to form a (2-vinyloxy)ethoxybenzaldehyde. The benzaldehyde is then condensed with nitromethane with an equimolar amount of potassium hydroxide to form a salt which upon acidification yields the desired β-nitrostyrene. This latter reaction was first reported by Thiele.[13]
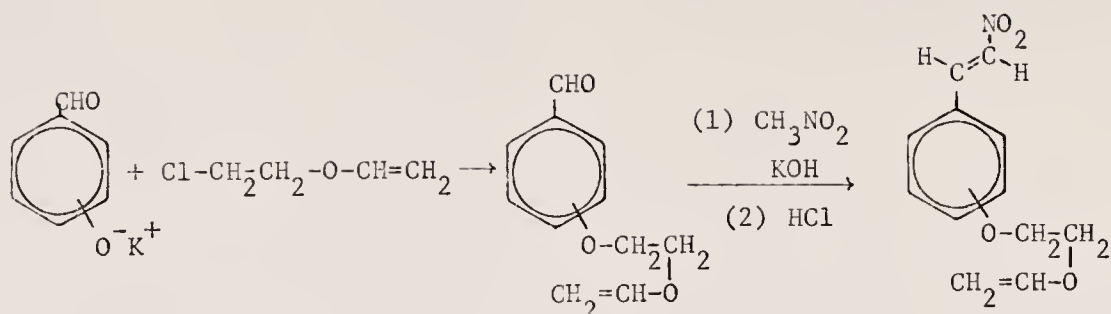
During Nash's study, he found that the meta and para isomers
polymerized readily in the presence of sodium methoxide. He also
noted that these monomers lacked the 1202 cm$^{-1}$ infra-red absorption
typical of vinyl ethers. These monomers were found to be resistant
to cationic polymerization upon reaction with $BF_3 \cdot Et_2O$. Nash con-
cluded that the two-stage polymerizations were "impractical" due to
the apparent reluctance of the vinyloxy groups to cationically poly-
merize.

Thompson[6] considered two possible explanations for the appar-
ent lack of reactivity toward electrophilic attack displayed by the
vinyl ether group on the para isomer. The first possibility he con-
sidered was an inductive effect. The resonance between the electron-
withdrawing nitro and the phenolic oxygen should lead to a signifi-
cant degree of positive charge on the oxygen due to the following
contributing resonance form:
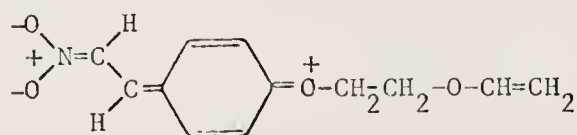
Electrophilic attack on the β-carbon of the vinyl ether would
produce a carbonium ion on the α-carbon which, in turn, would rely on
the lone-pair electrons on oxygen for resonance stabilization.

$$\begin{array}{c} ^-O \\ ^+N=C \\ ^-O \end{array} \begin{array}{c} H \\ C= \end{array} \bigcirc = \overset{+}{O}-CH_2CH_2-\overset{+}{O}=CH-CH_2-E$$
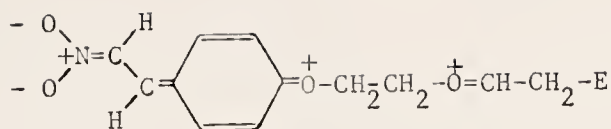
Consequently, the two contributing resonance forms would involve oxonium ions separated by a two-carbon saturated hydrocarbon bridge. The other possibility considered involved an intramolecular interaction between the terminal methylene of the vinyloxy group and the phenolic oxygen.

$$\begin{array}{c} ^-O \\ ^+N=C \\ ^-O \end{array} \begin{array}{c} H \\ C= \end{array} \bigcirc = \overset{+}{O} \begin{array}{c} ^-CH_2CH \\ CH_2CH_2 \end{array} O$$
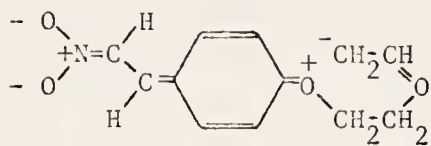
In considering the inductive factor, Thompson pointed out that the pKa of chloroacetic acid is 2.86 while that of β-chloropropionic acid is 4.00. The pKa of acetic acid is 4.80. This "quite minor" difference was considered to be evidence against the inductive effect.

Thompson then carried out an extensive and systematic study of the physical and spectral properties of the (2-vinyloxy)ethoxy-β-nitrostyrenes and related compounds in search of evidence. During this study, he clearly demonstrated that Nash's method of synthesis, which involved generation and precipitation of the (2-vinyloxy)ethoxy-β-nitrostyrene in excess dilute hydrochloric acid, resulted in the quantitative acid catalyzed hydrolysis of the vinyl ether group to the corresponding alcohol. Thompson modified the method of synthesis by lowering the reaction temperature and using only a slight excess of acid. Using these modifications, he successfully synthesized the ortho

and para isomers, although he was unsuccessful in isolating the meta isomer.

Thompson's spectral study included comparison of the ultra-violet spectra of para-(2-ethyloxy)ethoxy-β-nitrostyrene with the corresponding vinyl ether. Thompson observed no indication of an in-tramolecular interaction with those data.

Shostakovskii[13] postulated a mesomeric effect for vinyl ethers between the vinylic π-orbital and a lone-pair p-orbital on the oxygen. Since there are two such lone-pairs, such an effect would be expected to lead to rotational isomerism. Brey and Tarrant[14] observed 2 absorptions in the 1600-1650 $cm^{-1}$ region for vinyl ethers and attributed this to the existence of two rotational isomers.

Thompson pointed out that only one such rotational isomer would be present if the postulated intramolecular electrostatic attraction resulted in C being the sole existing conformation of the compound. He then obtained an infra-red spectrum of the compound using a Perkin-Elmer Model 21 double beam recording spectrophotometer and observed an absorption at 1621 $cm^{-1}$ but no absorption maximum between 1635 and 1660 $cm^{-1}$ Vinyl ethers normally possess a second but weaker absorption at 1640 $cm^{-1}$ in addition to the 1620 $cm^{-1}$ absorption. This was interpreted as supporting evidence for the intramolecular inter-action.

He obtained further data for the vinyloxyethoxy series as opposed to the ethyloxyethoxy series by experimentally determining the dipole moments in solution of each compound. The dipole moment for para-(2-vinyloxy)ethoxy-β-nitrostyrene was 5.43 D. as opposed to 6.14 D. for para-(2-ethyloxy)ethoxy-β-nitrostyrene. This difference was considered "significant."

Thompson concluded that his infra-red data indicated that the ring was the only form present, that his ultra-violet data indicated that the ring form (C) was probably not present, and that the dipole moment data indicated that there might be a contribution of the ring form.

## C. The Effect of Meta and Para-substituents on the Anionic Polymerization of β-nitrostyrenes

Little quantitative work has been done to study the effects of substituents on the reactions of β-nitrostyrenes. Worrall[15] found that β-nitrostyrene formed adducts with certain primary amines such as toluidine, phenyl hydrazine, aniline, and para-tolyhydrazine but was unreactive toward para-bromophenylhydrazine and ortho- and meta-toluidine. He also reported[16] that para-methyl-β-nitrostyrene, while not resistant to polymerization, was resistant to attack by all of the previously mentioned amines. However, nitration of the compound to meta-nitro-para-methyl-β-nitrostyrene was found to increase the reactivity of the compound. Addition products with aniline and para-toluidine were formed but the compound was still unreactive toward phenylhydrazine. Worrall later reported[17] that para-N,N-dimethylamino-β-nitrostyrene was not only resistant to reaction with the more reactive amines but also resistant to anionic polymerization.

Kamlet[18] has reported that barbituric acid reacts with certain β-nitrostyrenes in neutral or acidic media to form the corresponding 5-(2-nitro-1-aryl)-barbituric acids. The structures of the compounds thus synthesized were confirmed by oxidative degradation. Kamlet and Glover[19] later carried out a kinetic study of this reaction in a

buffered solution of dioxane in water. They demonstrated that the reaction was first order both in barbiturate anion (or barbituric acid) and β-nitrostyrene. They then obtained by ultra-violet analysis second order rate constants for β-nitrostyrene as well as for six substituted β-nitrostyrenes. A Hammett plot of this data appears in Figure 21.

No analogous study has been carried out to determine the effect of substituents on the rate of anionic polymerization of β-nitrostyrenes. Drueke[7] polymerized several substituted β-nitrostyrenes under identical conditions and, for the meta- and para-substituted compounds, observed no direct correlation between the expected reactivity of the compounds and the yield of polymer. In fact, he reported that para,β-dinitrostyrene, which he expected to be the most reactive of those tested, gave one of the poorest yields (7.93 percent sonversion). Meta,β-dinitrostyrene, also a relatively reactive compound, also gave a poor yield (1.45 percent conversion). Under identical reaction conditions, the much less reactive para-methoxy-β-nitrostyrene gave 65 percent conversion to ethanol insoluble polymer. No explanation was offered.

D. Effect of Ortho-substituents on the Rate of Polymerization on the Anionic Polymerization of β-nitrostyrenes

The reactivity of various ortho-substituted β-nitrostyrenes toward various primary amines has been quite extensively studied by Worall. He reported[20] that ortho-methoxy-β-nitrostyrene was unreactive toward all amines tested (as was the para isomer). However, nitration of the compound with fuming nitric acid gave a compound which he identified (probably incorrectly) as ortho-methoxy-para,β-dinitrostyrene. This compound reacted with para-toluidine to form a 1:1 adduct.

Ortho-chloro[21] and ortho-bromo-β-nitrostyrenes[22] were synthesized and each was also found to be unreactive toward all amines tested. However, nitration of each produced the corresponding 2-halo-5,β-dinitrostyrene. Both were observed to be more reactive toward amines than β-nitrostyrene, giving 1:1 adducts with ortho-, meta-, and para-toluidine. Ortho-iodo- -nitrostyrene[23] was also synthesized and studied. Worall found that, while the β-nitrostyrene was also unreactive, nitration of the compound to 2-iodo-5,β-nitrostyrene made the compound apparently more reactive toward amines than the corresponding chloro and bromo analogs. There was no apparent "ortho-effect" reported for this type of reaction and Worall made no comments as to the polymerizability of these compounds.

Apparently the first report of an "ortho-effect" was made when Nash[13] found that ortho-allyloxy-β-nitrostyrene and ortho-methoxy-meta-allyl-β-nitrostyrene both failed to give ethanol insoluble polymer upon addition of sodium methoxide. Later, Drueke[7] found that ortho-methoxy-, nitro-, and chloro--β-nitrostyrenes gave no ethanol insoluble polymers while ortho-fluoro-β-nitrostyrene gave 1.84 percent conversion to ethanol insoluble polymer. This effect was attributed to steric factors by that worker.

## Objectives of This Study

### A. Chemistry and Polymerization of (2-vinyloxy)ethoxy-β-nitrostyrenes

Thompson's successful synthesis of the ortho and meta isomers and his identification of the products of Nash's intended synthesis of these compounds suggested that these compounds might be excellent

monomers for two-stage polymerizations. One of the first objectives of this study was to test these compounds for such behavior. Such a development could lead to very practical applications. Monomeric β-nitrostyrenes have been found to be effective in combating bacteria,[24,25,26,27] fungi,[24,26,28] mold,[29] and insects.[26,28] The vapor pressure and solubility of many monomeric fungicides make them, at least mildly, hazardous to the environment. However, if such a biologically active moeity were pendant on a polymer chain of reasonably high molecular weight, it would have the ecological advantage of being essentially immobile. The successful cationic polymerization of any of the three isomers of the vinyloxyethoxy-β-nitrostyrenes would lead to such a polymer.

$$NO_2$$
$$H-C=C-H$$

$$O$$
$$CH_2$$
$$CH_2$$
$$O$$
$$RO(CH-CH_2)_x H$$
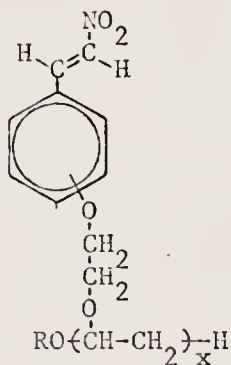
It was also felt that the postulated ring form for the para isomer was worthy of more study. Despite the fact that Thompson proved that the para isomer, as synthesized by Nash (with vinyl ether moeity no longer present), could not have cationically polymerized, his spectral and physical data seemed to indicate that such a form might still be a contributing form or the sole form of the compound.

The uncommonly high dipole moment of the compound as determined

by Thompson indicates that there must be a significant amount of positive charge on the phenolic oxygen. The nmr spectra of vinyl ethers indicates that there is a significant amount of negative character on the terminal carbon as evidenced by the relatively high field chemical shift of the terminal protons.[30] Banwell and Sheppard[31] have attributed this effect directly to the mesomeric effect since electron donation through resonance interaction leads to increased electron density on the terminal methylene carbon. This is due to the fact that the magnetically anistropic $\pi$ electrons are distributed over 2 bonds rather than one.

Thus with considerable positive charge on the phenolic oxygen and some degree of negative charge on the terminal methylene, the postulated 6-membered ring would appear to be a viable possibility.

One of the first objectives of this study was the successful synthesis of the meta isomer to permit careful comparison of the chemical and physical characteristics of the two compounds. If the inductive effect is the predominant effect on the chemical and physical behavior of para-(2-vinyloxy)ethoxy-$\beta$-nitrostyrene, then one would expect a decreased mesomeric effect in the para isomer as compared to the meta isomer. On the other hand, the contribution of the ring form would be expected to increase the degree of the mesomeric effect relative to the meta isomer.

Theoretical work by Gutowski, Karplus, and Grant[32] followed by a systematic nmr study of vinylic compounds by Banwell and Sheppard has shown that the coupling constants, particularly the geminal coupling constant ($J^{gem}$), are quite sensitive to inductive effects. The latter work indicated that in the case of monosubstituted vinylic

compounds, there is a definite correlation between the electronegativity of the substituent and the geminal coupling constants of the terminal methylene protons and that decreasing coupling constants go with increasing electronegativity. These findings gave excellent agreement with theoretical predictions. Geminal coupling constants for vinyl halides ranged from -3.2 hz. for vinyl fluoride to -1.7 hz. for vinyl bromide.

Later work by Feeney, Ledwith, and Sutcliffe[33] applied this type of analysis to vinyl ethers. In the case of simple vinyl ethers,

$$R-O-CH=CH_2 \quad \longleftrightarrow \quad R-\overset{+}{O}=CH-\overset{-}{C}H_2$$
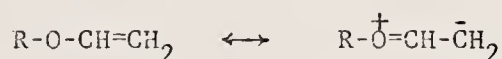
the inductive effects of various alkyl groups were expected to exert an influence on the extent of mesomeric stabilization and, in turn, on the amount of carbanion character on the terminal methylene. Their data, which appear in Table 6a, for vinyl ethers. in which the R was a single saturated alkyl substituent, showed that as the electron donating (inductive) ability of the substituent increased so did the geminal coupling constant. The values obtained ranged from $J^{gem} = -0.1$ hz. for t-butyl vinyl ether to $J^{gem} = -2.2$ hz. for methyl vinyl ether. β-chloroethyl vinyl ether was found to have a geminal constant of -2.7 hz.

The apparent sensitivity of the coupling constants to the character of the substituents suggested that a detailed nmr study of the (2-vinyloxy)ethoxy substituted β-nitrostyrenes might help clarify the question.

A thorough analysis of the infra-red spectrum of the three isomers of the (2-vinyloxy)ethoxy-β-nitrostyrenes as well as related compounds appeared desirable as well. It is interesting to note that

Feeney, Ledwith, and Sutcliffe[33] saw no indication of rotational isomer-ism for 2-ethylhexyl vinyl ether between temperatures of $-100^{\circ}$ and $100^{\circ}$ C. in their nmr study in contrast to the infra-red work of Brey and Tarrant.[14]

## B. Effect of Meta and Para-substituents on the Rate of Anionic Polymer-izations of Certain β-nitrostyrenes

A study was also initiated during the course of this work to obtain some quantitative data concerning the effect of meta and para-substituents on the rates of anionic polymerizations of β-nitrostyrenes. The rates of polymerization were determined by a gravimetric method. The rates of initiation of two representative monomers were obtained spectroscopically.

The process of initiation in an anionic polymerization may be expressed as $I^-A^+ + M \xrightarrow{k_i} I-M^-A^+$, where:

$\bar{I}$ is the initiating species

$A^+$ is the counterion or gegnion

M is the monomer

$k_i$ is the rate constant of initiation

The over-all rate of initiation may be expressed in the form $\nu_i = k_i[I^-][M]$.

The process of propagation may be expressed as

$R-(M)_x^-M^-A^+ + M \xrightarrow{k_p} R-(M)_{x+1}M^-A^+$. where:
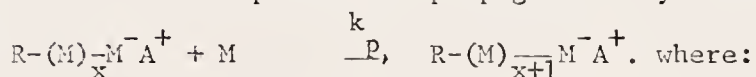
$R-(M)_x^-M^-$ is the growing polymer molecule

$k_p$ is the rate constant of propagation

The rate of propagation may then be expressed[34] as

$\frac{-d[M]}{dt} = \nu_p = k_p[M^-][M]$, where $M^-$ refers to the concentration of actively propagating anions. It was assumed in this study that the above

relationship adequately described the over-all rate of polymerization of certain mono-substituted β-nitrostyrenes. This required that the following assumptions be made:

1. The rate of initiation is fast relative to the rate of propagation.

2. The rate of chain transfer is small or non-existent relative to the rate of propagation and, if it does occur, it does not alter the kinetic chain.

3. Auto-termination does not occur during the polymerization.

4. The length of the polymer chain does not affect the rate of propagation.

5. The rate of propagation remains essentially unchanged during both the homogeneous and heterogeneous stages of the polymer-ization.

6. Conversion of initiator to propagating carbanion is quantitative and the reactivity of all resulting ion-pairs is assumed to be equal.

7. The rate of polymerization equals the rate of disappear ance of monomer; $v_p = -\frac{d[M]}{dt} = \frac{d[P]}{dt}$, where P is polymer yield expressed in terms of moles of monomer units/liter of solution. This assumption precludes any significant side-reactions, e.g., the base catalyzed Michael addition of ethanol to β-nitrostyrene.

Assumption 7, if valid, permits the rate of polymerization to be monitored gravimetrically by weighing the precipitated polymer. This approach, in turn, requires that precipitation of polymeric product be essentially quantitative.

The Hammett equation has been used to a limited extent in mechanistic polymer chemistry. The treatment has been used to study

the free radical polymerization of styrene,[35] cationic polymerizations

of styrenes[36,37] and phenyl ethers,[38] Ziegler-Natta polymerization of

styrenes,[39] and reaction of polystyryl anions with styrenes.[40]

The Hammett equation was applied to this study using the form

$\log k_p/k_o = \sigma\rho$, where $k_p$ is the second order propagation rate constant

of a substituted-β-nitrostyrene and $k_o$ is the propagation rate constant

of unsubstituted-β-nitrostyrene. Hammett treatment would permit quan-

titative comparison of the Michael reaction[19] and anionic polymeriza-

tion of β-nitrostyrenes. Since the rate-determining step of the

Michael reaction, like anionic polymerization, is said to involve at-

tack of the anion on substrate[41] one might expect similar results.

A kinetic study of the anionic polymerization of the ortho-

substituted-β-nitrostyrenes was also undertaken. It was hoped that

such a study might clarify whether or not the effect observed by Nash[13]

and Drueke[7] was purely steric as well as distinguish between the two

possibilities of steric inhibition of initiation and steric inhibition

of propagation.

A very brief and superficial study was carried out to deter-

mine the extent of chain transfer and/or termination by studying the

molecular weight distributions of some of the representative polymers

obtained during the kinetic studies.

It should be noted that all anionic polymerizations were

carried out in a protic solvent system. In most cases of anionic

polymerization, the presence of a protic compound, even in small con-

centration, leads either to termination or chain transfer. Volker[42]

found that by varying the concentration of methanol, he could vary the

molecular weight of polymer obtained from the anionic polymerization

of methyl methacrylate.  By increasing the concentration of chain
transfer agent (methanol), he could quite precisely lower the molecu-
lar weight of product polymer.

Szarc and coworkers,[43,44,45] on the other hand, reported that
anionic polymerization of vinylic compounds which formed "living poly-
mers" led to the formation of polymers having very narrow molecular
weight distributions.  These polymerizations were run in scrupulously
dry aprotic solvents under an inert atmosphere or high vacuum.

The molecular weight distribution of a given polymer sample
can be obtained by one of the several known laborious methods of mole-
cular weight fractionation such as ultra-centrifugation,[46] fractional
precipitation,[47] sequential extraction,[48] dialysis,[49] and several others.
The worker then determines the molecular weight of each polymer frac-
tion obtained.  The recent advent of practical gel permeation chroma-
tography (GPC), as applied to polymer chemistry,[50,51] has provided an
analytical, as well as preparative, tool for rapid fractionation and
determination of molecular weight distribution curves.

Briefly, this method separates different molecular weight
polymer molecules on the basis of molecular size.  A polymer solution
is passed through a column containing insoluble porous gel particles.
The longer polymer molecules, whose physical size effectively prevents
their diffusion into the gel pores, pass more quickly through the
column by passing between the gel particles with the solvent flow.  The
smaller polymer molecules spend more time diffusing in and out of the
gel pores and consequently travel more slowly through the gel.  Upon
leaving the column, the fractionated solution passes through an ultra-
violet photometer and/or a differential refractometer.  Thus, the

recorded signals from these detectors are molecular weight distribution curves.

The recorder also records the volume of solvent passing through the column during a given run in the form of 5 ml. "count" marks. The volume of solvent required to elute a given polymer size is extremely characteristic of that size. Thus, a calibration curve derived from standard polymer samples of known molecular weight and size can be used to determine number average molecular weights and lengths of a given polymer sample of the same type polymer, e.g., polystyrene.

# CHAPTER II

## EXPERIMENTAL

### Synthesis and Chemistry of Ortho-, Meta-, and Para-(2-vinyloxy)ethoxy-β-nitrostyrenes

A. Preparation of the (2-vinyloxy)ethoxy-substituted β-nitrostyrenes

These compounds were synthesized by the method of Thompson
with some slight modifications in the work-up procedure.

1. Ortho-(2-vinyloxy)ethoxy-β-nitrostyrene.-- The potassium
salt of salicylaldehyde was prepared on a 0.2 mole scale by reacting
24.41 g. of salicylaldehyde (in 20 mls. of absolute ethanol) with 13.20
g. of 85 percent potassium hydroxide dissolved in 140 mls. of absolute
ethanol. The solvent was then removed by distillation under vacuum.
Any remaining water was removed via the benzene-water azeotrope. The
yellow crystalline product was then dried under vacuum for 24 hrs. The
yield was essentially quantitative and the hygroscopic salt was used
immediately.

The potassium salt was dissolved in 120 mls. of dimethyl-
formamide which had been dried over 4Å molecular sieves. To this
solution was added 0.2 mole plus 10 percent excess of β-chloroethyl
vinyl ether. The solution was refluxed gently for 24 hrs. with stir-
ring. After the reaction mixture had cooled to room temperature, suf-
ficient deionized water was added to dissolve the precipitated potas-
sium chloride. The product was then extracted with ether and the
ethereal solution was dried with anhydrous magnesium sulphate. The

ether was removed by vacuum distillation at room temperature and the
ortho-(2-vinyloxy)ethoxy-benzaldehyde was then purified by distilla-
tion (110°C. at 0.17mm Hg) yielding 28.8 g. (75 percent yield) of the
light yellow oil. The spectral and physical properties of the product
agreed with those of Thompson.

The corresponding β-nitrostyrene was synthesized via a modi-
fied Thiele reaction. The compound was synthesized on a 0.113 mole
scale. 21.64 g. of the benzaldehyde were placed in a 250 ml. erlen-
meyer flask with 100 mls. of absolute methanol and 6.1 mls. (0.113
mole) of nitromethane. This solution was chilled in an ice-methanol
bath (with magnetic stirring) to -5°C. To this solution was added,
dropwise, 22.5 mls. of 5.0 M. potassium hydroxide in water (0.113
mole). The potassium hydroxide solution was added at such a rate that
the temperature was not allowed to exceed 0°C. The solution was then
stirred at the same temperature for an additional 10 minutes. The
solution was then added to about 30 g. of ice in a 250 ml. separatory
funnel and the ice was allowed to melt with occasional swirling. The
resulting solution was added dropwise to a vigorously stirred mixture
of 75 g. of ice, 100 mls. of water, and 11 mls. of 37 percent HCl
(0.113 mole plus slight excess). Ice was added during this step as
needed to keep the mixture cold. The resulting yellow precipitate
was quickly filtered and washed with 500 mls. of chilled deionized
water to remove excess HCl. The crude product was then immediately
dissolved in a minimum amount of methylene chloride (about 150 mls.)
and placed in a separatory funnel. The bottom layer (methylene chlo-
ride and product) was then filtered through a 5.5 cm. Buchner funnel
half-filled with anhydrous $MgSO_4$. The resulting clear, yellow solution

was placed in a large crystallizing dish along with 250 mls. of absolute ethanol. The resulting solution was then partially evaporated at room temperature under a stream of nitrogen which had been passed through a drying tube filled with anhydrous $CaSO_4$. This resulted in the formation of a large amount of long thin needles. Filtration under vacuum produced 18.90 g. of the desired product, m.p.: 62-62.5°C. Further evaporation under nitrogen followed by chilling to -15°C. produced 2.96 g. of product, m.p.: 60-60.5°C. The percent yield obtained (cumulative) was 89 percent. The melting point of the first crop agreed perfectly with that reported by Thompson.

2. <u>Meta-(2-vinyloxy)ethoxy-β-nitrostyrene</u>.-- The corresponding meta-(2-vinyloxy)ethoxybenzaldehyde was prepared in a manner entirely analogous to that for the previous monomer on a 0.3 mole scale. 41.83 g. (73 percent yield) of colorless liquid were obtained by vacuum distillation, b.p.: 94°C. at 0.17 mm Hg. This benzaldehyde crystallized to form colorless needle crystals, m.p.: 41-42°C. The physical characteristics agreed with those reported by Thompson and the spectroscopic data supported the structure.

Attempts to synthesize meta-(2-vinyloxy)ethoxy-β-nitrostyrene by the method of Thompson produced good yields of a yellow crystalline material, m.p.: 113-113.5°C. Nash's reported melting point was 112-113°C. for this compound. Thompson demonstrated that this compound was actually meta-(2-hydroxy)ethoxy-β-nitrostyrene, the product of acid catalyzed hydrolysis of the corresponding vinyl ether.

A repeated attempt was made to synthesize this compound by Thompson's method with certain modifications as described in the previous synthesis. After the yellow precipitate was filtered and washed

with chilled deionized water, an nmr spectrum of the crude product indicated that the vinyloxy group was still intact. Recrystallization from ethanol and water as described by Thompson gave the alcohol exclusively. The synthesis was repeated on a 0.0328 mole scale and the crude product was dissolved in a minimum amount of $CCl_4$ (50 mls.), placed in a separatory funnel, and the lower layer filtered through anhydrous $MgSO_4$. The superficially dried solution was then chilled to $-15^{\circ}C$. for 48 hrs. during which time many small "nodules" of bright yellow product formed. These were scraped loose with a spatula, filtered, and dried under vacuum for 12 hrs. at room temperature yielding 6.95 g. (90 percent yield) of the desired product, m.p.: $53-53.5^{\circ}C$.

The nmr spectrum ($CDCl_3$) of the compound, which is shown in Figure 2, included a 2-proton AB quartet for the nitrovinyl protons, $\tau H_A = 1.98$, $\tau H_B = 2.45$ ($J_{AB} = 14.2$ hz.); a 4-proton multiplet for the aromatic protons, $\tau = 2.48-3.10$; a 1-proton quartet for the $\alpha$-proton on the vinyloxy group, $\tau = 3.46$ ($J_{\alpha\beta \ cis} = 6.9$ hz., $J_{\alpha\beta \ trans} = 14.2$ hz.); and a 6-proton multiplet for the ethoxy group and the $\beta$-protons of the vinyloxy group, $\tau = 5.56-6.06$. The infra-red spectrum of the compound included absorptions at 1620 and 1640 $cm^{-1}$ strong and sharp, $\nu$ C=C in vinyloxy group; 1610 and 1601 $cm^{-1}$ medium and sharp, $\nu$ C=C in aromatic group; 1640 $cm^{-1}$ overlapping with 1640 $cm^{-1}$ absorption from vinyloxy group, $\nu$ C=C in nitrovinyl group. This assignment was made by comparison of the spectrum with that of meta-methoxy-$\beta$-nitrostyrene. The ultra-violet spectrum in ethanol was characterized by an absorption at $\lambda_{max.} = 304$ m$\mu$ ($\varepsilon = 12,500$); and $\lambda_{max.} = 246$ m$\mu$ ($\varepsilon = 33,600$).

3. <u>Para-(2-vinyloxy)ethoxy-$\beta$-nitrostyrene.</u>-- The benzaldehyde was prepared on a 0.5 mole scale by the method of Thompson. Vacuum
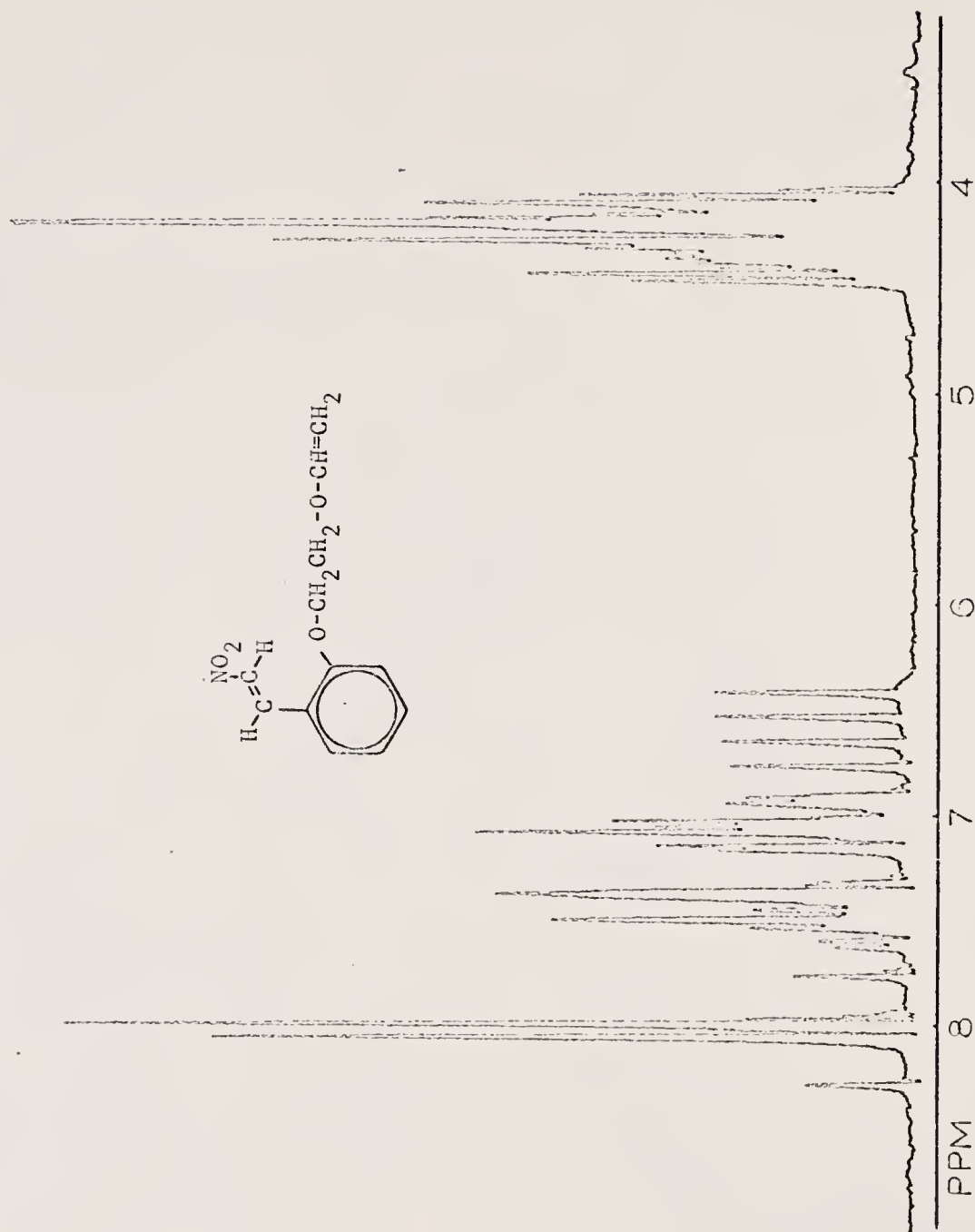
Figure 1

NMR Spectrum of Ortho(2-vinyloxy)ethoxy-β-nitrostyrene
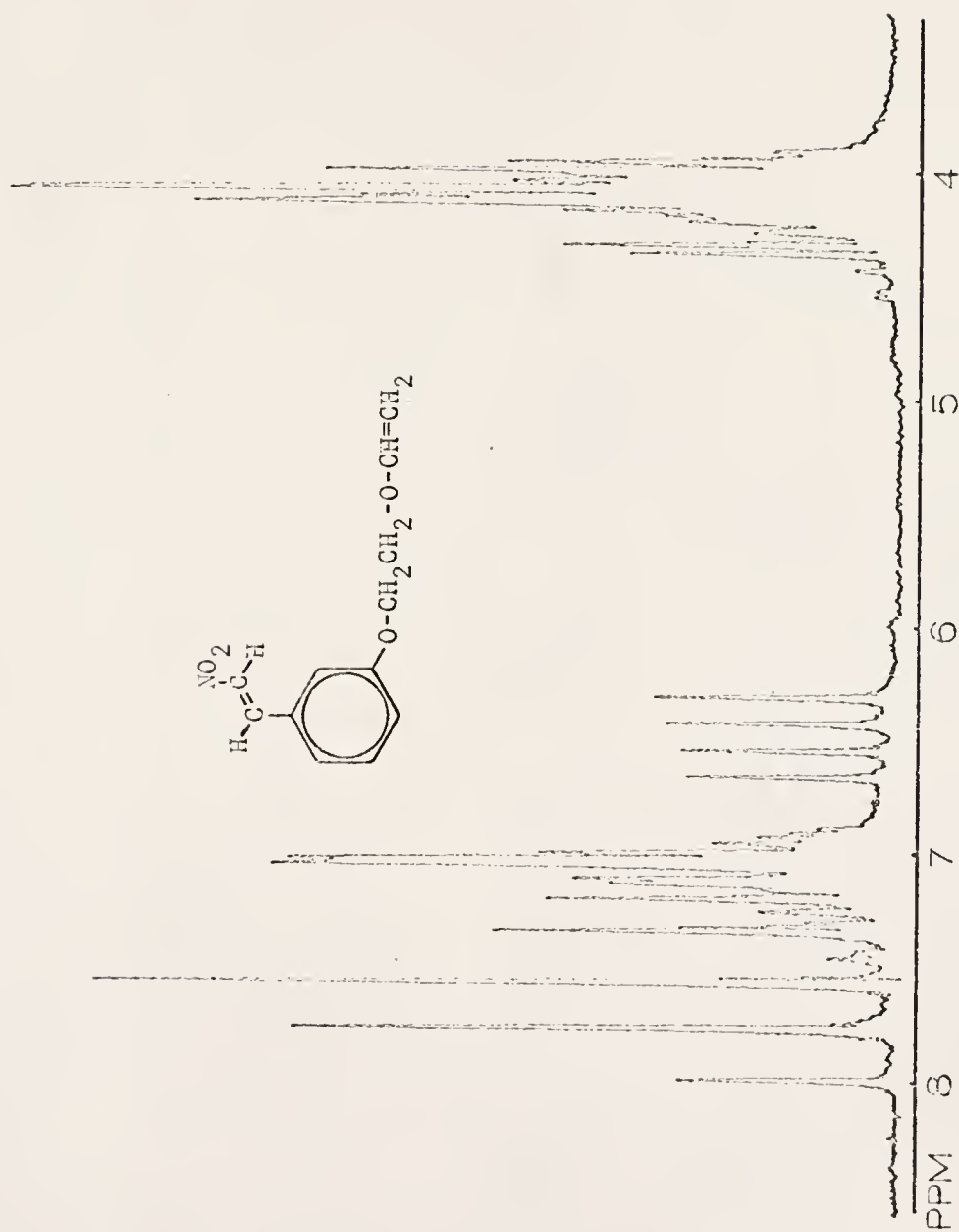
Figure 2

NMR Spectrum of Meta-(2-vinyloxy)ethoxy-β-nitrostyrene
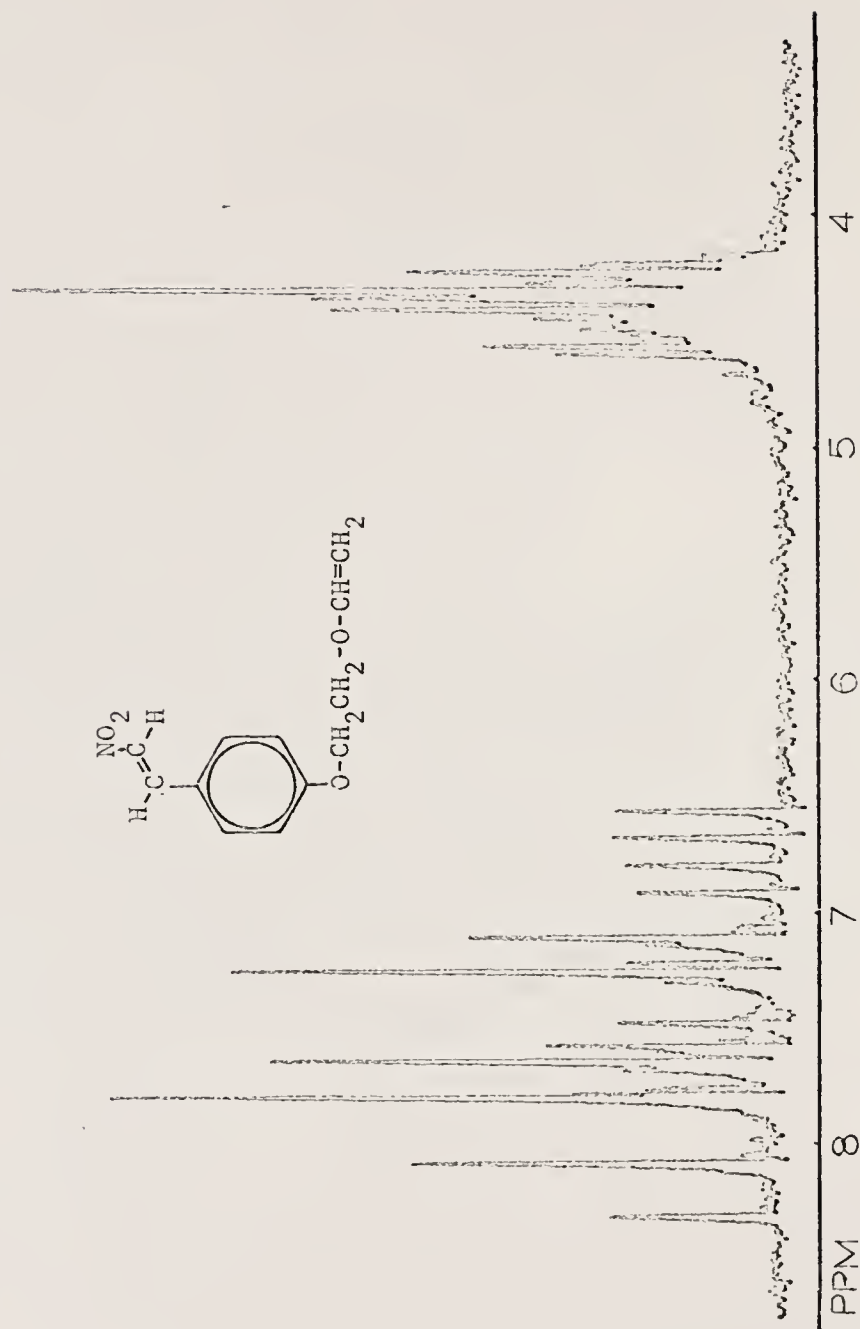
Figure 3

NMR spectrum of Para-(2-vinyloxy)ethoxy-β-nitrostyrene

distillation of the crude product (b.p.: $110^{\circ}$C. at 0.2 mm H$_3$) yielded 88.6 g. (92.5 percent yield) of colorless oil. The physical properties agreed well with those reported by Thompson and the spectral proper-ties supported the proposed structure.

The β-nitrostyrene was synthesized on a 0.037 mole scale using the previously described method. The crude product was dissolved in a minimum amount of CH$_2$Cl$_2$ (100 mls.) at room temperature, filtered, and added to 150 mls. of 95 percent ethanol. The resulting solution was partially evaporated under a stream of air and chilled to $-15^{\circ}$C. After 24 hrs., the yellow needle crystals were filtered and dried under va-cuum. 12.30 g. (60 percent yield) of purified product were obtained, m.p.: $103-103.5^{\circ}$C. This value agreed well with that reported by Thompson.

## B. Cationic Polymerization Studies of the (2-vinyloxy)ethoxy-substitu-ted β-nitrostyrenes

1. Cationic polymerization of para-(2-vinyloxy)ethoxy-β-nitro-styrene. -- The polymerization of this monomer was conducted on a 1.356 g. scale. The monomer was dissolved in 125 mls. of methylene chloride and polymerized with 5 mls. of BF$_3$ gas (4 mole percent). 0.865 g. (64 percent conversion) of deep yellow amorphous polymer was obtained by precipitation in methanol. The infra-red spectrum included a fairly strong absorption at 1630 cm$^{-1}$ which was assigned to the nitrovinyl moeity after comparison with the infra-red spectrum of para-methoxy-β-nitrostyrene. The intrinsic viscosity in methylene chloride was 0.21 dl/g. The molecular weight was determined to be $\overline{M}_n = 5.2 \times 10^3$ using a Mechrolab vapor pressure osmometer. The melt temperature of the poly-mer was $120-125^{\circ}$C.

The above polymer was cross-linked by reacting a solution of 0.5 g. of the polymer in 20 mls. of dry methylene chloride with 0.5 ml. of sodium ethoxide in ethanol (1 mmole/ml.). Conversion to insoluble material was complete. The infra-red spectrum of the grayish material included an absorption at 1608 cm$^{-1}$ for the aromatic nucleus; but no absorption at 1630 cm$^{-1}$ was apparent, indicating that reaction of the nitrovinyl groups was essentially complete. The insoluble polymer gave a melt temperature of 235$^{\circ}$C. with decomposition.

2. <u>Cationic polymerization of meta-(2-vinyloxy)-ethoxy-β-nitrostyrene</u>.-- The cationic polymerization of the meta isomer was effected using a similar procedure. One gram of monomer was polymerized in 30 mls. of dry methylene chloride using 1 mole percent BF$_3$. 0.083 g. of methanol insoluble polymer (8.3 percent conversion) was obtained. The infra-red spectrum of the polymer contained an absorption at 1602 cm$^{-1}$ which was assigned to the aromatic nucleus, and an absorption at 1640 cm$^{-1}$ for the pendant nitrovinyl moeity. The intrinsic viscosity of the polymer was 0.14 dl/g. in methylene chloride and the melt temperature of the amorphous yellow polymer was 85-95$^{\circ}$C.

This polymer was cross-linked by dissolving 0.5 g. of the above polymer in 20 mls. of dry methylene chloride and reacting the polymer with 0.05 ml. of sodium ethoxide in ethanol (1 mmole/ml.). Conversion to insoluble material was quantitative. The infra-red spectrum included a broad absorption at 1600 cm$^{-1}$ which was assigned to the aromatic nucleus and a shoulder at 1640 cm$^{-1}$ which indicated that the reaction of the nitrovinyl group was not complete. The amber-colored polymer gave no melt temperature up to 260$^{\circ}$C. although it discolored at about 250$^{\circ}$C.

3. <u>Cationic polymerization of ortho-(2-vinlyoxy)ethoxy-β-nitrostyrene.</u>-- 2.35 g. of monomer were placed in a 250 ml. erlenmeyer flask which had previously been flamed and cooled. A serum cap was placed on the flask and wired in position. A hypodermic needle was placed in the cap to serve as a vent during evacuation of the vessel in the vacuum chamber of the Dri-Lab. After evacuation, the atmosphere in the vessel was replaced with dry $N_2$ in the Dri-Lab and the needle removed. The flask was removed from the Dri-Lab and 50 mls. of $CH_2Cl_2$, which had been redistilled and dried over 3$\overset{\circ}{A}$ molecular sieves, were added. The flask was then placed in an isopropanol-dry ice bath and chilled to -75$^\circ$C. 7 mls. of $BF_3$ gas (3 mole percent) were then introduced with a hypodermic syringe. There was an instant flash of red on the surface of the solution which dissappeared upon vigorous swirling. After 30 minutes the light amber solution was added dropwise, through a filter, into 75 mls. of vigorously stirred methanol. The flocculent yellow polymer was filtered and dried under vacuum. Conversion to polymer was essentially quantitative. The melt temperature of the polymer was 90-100$^\circ$C. and its intrinsic viscosity was 0.25 dl/g. The infra-red spectrum of the polymer was characterized by the lack of the strong 1620 cm$^{-1}$ peak from the C=C stretch of the vinyl ether and the presence of a weak peak at 1625 cm$^{-1}$ for the C=C stretch of the β-nitrostyrene moiety.

An attempt to cross-link this polymer by the previously described method gave no significant amount of precipitate.

C. <u>Anionic Polymerization Studies of (2-vinlyoxy)ethoxy-substituted β-nitrostyrenes</u>

1. <u>Anionic polymerization of meta-(2-vinyloxy)ethoxy-β-nitrostyrene</u>.-- 1.95 g. of monomer were placed in a 60 ml. erlenmeyer flask and dissolved in 40 mls. of 50 percent THF in absolute ethanol. 0.08 ml. of sodium ethoxide in ethanol solution (1 mmole/ml.) was added and the solution stirred at $25^{\circ}$C. for 24 hrs. The precipitated polymer was centrifuged and washed twice with methanol. The polymer was then dried under vacuum for 24 hrs. 1.26 g. (64 percent conversion) of white powdery polymer were obtained. The product was found to be insoluble in all common organic solvents tried but soluble in N,N-dimethylaniline and hexamethylphosphotriamide (HMPA). The intrinsic viscosity of the polymer in HMPA at $28^{\circ}$C. was 0.08 dl/g. The infra-red spectrum of the polymer indicated that the vinyl ether group was still intact (absorptions at 1620 cm$^{-1}$ and 1640 cm$^{-1}$). It was also interesting to note that on extended contact with air at room temperature the polymer became completely insoluble in all solvents tried including HMPA, apparently due to cross-linking through the pendant vinyloxy groups. The infra-red spectrum of the polymer showed that at least some of the vinyloxy groups were yet intact as indicated by the continued presence of the 1620 cm$^{-1}$ and 1640 cm$^{-1}$ absorptions.

2. <u>Anionic polymerization of para-(2-vinyloxy)ethoxy-β-nitrostyrene</u>.-- 2.35 g. (10 mmoles) of monomer were dissolved in 50 ml. of 60 percent THF in absolute ethanol. The polymerization was carried out as described for the meta isomer. 1.54 g. (65.5 percent conversion) of white powdery polymer were obtained. The intrinsic viscosity of the polymer was 0.07 dl/g. in HMPA at $23^{\circ}$C. It decomposed at $235^{\circ}$C.

The vinyloxy groups were once again left intact as indicated by infra-red absorptions at 1620 cm$^{-1}$ and 1640 cm$^{-1}$. A sample of this

polymer, which had been stored in non-dried air for an extended period, was found to be insoluble in HMPA indicating some cross-linking. Both absorptions were still present in the infra-red indicating the presence of some yet unreacted vinyloxy groups.

3. <u>Attempted anionic polymerization of ortho-(2-vinyloxy)-ethoxy-β-nitrostyrene</u>.-- This monomer did not polymerize in the presence of sodium ethoxide. Monomer was recovered almost quantitatively after an attempted polymerization using the above described method.

D. <u>Analysis of the Conformation of Para-(2-vinyloxy)ethoxy-β-nitro-styrene</u>

1. <u>Ultra-violet analysis</u>.-- The ultra-violet spectrum of the para isomer in methylene chloride ($5 \times 10^{-5}$ M.) was obtained as was the spectrum of the cationically initiated polymer ($1 \times 10^{-4}$ M. expressed as concentration of monomer units). The spectrum could not be taken below 230 mμ due to solvent absorption. Both spectra appear in Figure 5, page 65. The spectrum of the monomer included absorption maxima at $\lambda_{max.} = 263$ mμ ($\varepsilon = 9,700$) and $\lambda_{max.} = 300$ mμ ($\varepsilon = 12,300$). The spectra of the polymer included absorption maxima at $\lambda_{max.} = 263$ mμ ($\varepsilon' = 5,120$) and $\lambda_{max.} = 300$ mμ ($\varepsilon' = 5,900$) where $\varepsilon'$ is defined in terms of concentration of monomer units.

2. <u>Synthesis of para-nitro-(2-vinyloxy)ethoxy benzene</u>.-- 10.12 g. (0.073 mole) of para-nitrophenol were dissolved in 100 mls. of absolute ethanol in a 500 ml. round-bottom flask. To this solution was added a solution of 9.10 g. of 85 percent potassium hydroxide dissolved in 100 mls. of absolute ethanol. Yellow crystals formed immediately. The solvent was removed by distillation under vacuum with

warming. Any remaining water was removed as the benzene-water azeo-
trope.

The salt was then reacted with β-chloroethyl vinyl ether in
dimethylformamide in the previously described manner. After 12 hrs.
of reaction time, the resulting mixture was chilled in an ice-water
bath and added to 200 mls. of ether in a separatory funnel. This mix-
ture was extracted twice with 150 ml. aliquots of chilled 2 percent
aqueous potassium hydroxide and once with 200 mls. of chilled deionized
water. The ethereal layer was then filtered through anhydrous magne-
sium sulphate and the solvent was then removed by distillation under
vacuum at room temperature. The tan solid was then dissolved in a
minimum amount of methylene chloride in a crystallizing dish and to
this was added 100 mls. of absolute ethanol. The methylene chloride
was then evaporated off under a stream of dry nitrogen with no warming.
This procedure yielded 8.72 g. (64.6 percent yield) of light tan crys-
tals, m.p.: 73-74°C. Recrystallization of the product by the same
method gave 6.47 g. (75 percent recovery) of white crystals, m.p.:
73-74°C. The infra-red and nmr spectra supported the proposed struc-
ture.

3. Infra-red analysis.-- The infra-red spectrum of para-
(2-vinyloxy)ethoxy-β-nitrostyrene in methylene chloride, as well as in
a potassium bromide pellet, was obtained. Both spectra contained absorp-
tions at 1199 cm$^{-1}$ (ν C-O of vinyloxy group), 1620 cm$^{-1}$ (ν C=C vinyloxy
group), 1630 cm$^{-1}$ (ν C=C nitrovinyl group), and a barely perceptible
shoulder at 1640 cm.$^{-1}$ The shoulder was assigned to the vinyloxy group
as well. This assignment was confirmed by obtaining the infra-red spec-
trum of para-nitro-(2-vinyloxy)ethoxybenzene. The lack of the

nitrovinyl absorption facilitated the observation of both the 1620 and 1640 cm$^{-1}$ absorptions typical of vinyl ethers. Major absorptions of these spectra as well as that of β-chloroethyl vinyl ether appear in Figure 4, page 61. This and other data appear in Table 5, page 62.

4. <u>Nuclear magnetic resonance analysis</u>.-- The nmr spectra of ortho-, meta-, and para-(2-vinyloxy)ethoxy-β-nitrostyrenes, para-nitro-(2-vinyloxy)ethoxybenzene, (2-vinyloxy)ethoxybenzene, and β-chloroethyl vinyl ether were obtained in deuterated chloroform. The spectra of the vinyloxy groups (50 hz. sweepwidth, 250 sec. speed) were analyzed in detail. Each spectrum was run twice of more to insure reproducibility. Part of the spectrum of the terminal methylene group was found to overlap with the spectrum of the ethyloxy group making complete analysis impossible. However, the low field half of the AB quartet assigned to H$_B$ (trans to the α-proton) was not subject to interference; hence, the geminal coupling constant could be obtained for each vinyloxy group. These constants and other data appear in Table 6a, page 63.

<div align="center">

<u>Studies of the Anionic Polymerization of Some<br>
Mono-substituted β-nitrostyrenes</u>

</div>

## A. <u>Synthesis of Substituted β-nitrostyrenes</u>

Fifteen substituted β-nitrostyrenes and β-nitrostyrene were synthesized for this study. Since the procedure for synthesis of these compounds was the same as that previously described for ortho(2-vinyloxy)ethoxy-β-nitrostyrene, it will not be described in full here. However, due to widely differing polarities of the various compounds, the crude products were recrystallized using different solvent systems.

The method of work-up will be described for each compound for this reason.

1. <u>β-nitrostyrene</u>.-- This compound was prepared on a 0.25 mole scale. The crude product was recrystallized twice from warm 95 percent ethanol to give 13.7 g. (37 percent overall yield) of yellow needle crystals, m.p.: 56-57°C. (lit.[12] 56-57°C.).

2. <u>Meta-methoxy-β-nitrostyrene</u>.-- This isomer was prepared on a 0.10 mole scale. The crude product was recrystallized once from warm ethanol. The yield was 10.29 g. (57.5 percent yield) of pale yellow plates, m.p.: 90-92°C. (lit.[52] 92°C.).

3. <u>Para-methoxy-β-nitrostyrene</u>.-- This monomer was synthesized on a 0.10 mole scale. The crude product was recrystallized from hot 95 percent ethanol. The yield was 13.02 g. (72.6 percent yield) of bright yellow plates, m.p.: 86-86.5°C. (lit.[53] 83°C.).

4. <u>Ortho-methoxy-β-nitrostyrene</u>.-- This styrene was also prepared on a 0.10 mole scale. The crude product was recrystallized from warm 95 percent ethanol and water giving 10.72 g. (60.2 percent yield) of yellow needles, m.p.: 47-48°C. (lit.[20] 47-48°C.).

5. <u>Meta-methyl-β-nitrostyrene</u>.-- This compound was synthesized on a 0.208 mole scale. The crude product solidified as usual in the last step of the synthesis when the reaction mixture was added dropwise to water, ice, and hydrochloric acid. Water is eliminated from the condensation product in this step. After the solid yellow material was filtered and washed with deionized water as usual, the product was found to liquify at room temperature. As a result the compound was purified by vacuum distillation to yield 18.67 g. (55 percent yield) of yellow oil, b.p.: 80°C. at 0.15 mm Hg, (lit.[54] 133° at 2.8 mm Hg), $n_D^{25} = 1.625$.

6.  **Para-methyl-β-nitrostyrene.**-- This compound was synthesized on a 0.25 mole scale. The crude product was dissolved in a minimum amount of hot 95 percent ethanol, filtered, and chilled to 0.15°C. for 24 hrs. The yield was 25.1 g. (62.5 percent) of lovely yellow needles, m.p.: 101.5-102°C. (lit.[16] 102°C.). Subsequent recrystallization failed to change the melting point.

7.  **Ortho-fluoro-β-nitrostyrene.**-- This compound was synthesized by the method of Thompson on a 0.20 mole scale. The crude product was recrystallized from ethanol and water yielding 15.40 g. (46 percent yield) of product, m.p.: 53-54°C. (lit.[54] 54°C.).

8.  **Meta-fluoro-β-nitrostyrene.**-- This monomer was synthesized on a 0.085 mole scale. The crude product was recrystallized from warm 95 percent ethanol by chilling to -15°C. The crystalline product was filtered and dried under vacuum yielding 7.19 g. (50.6 percent yield) of product, m.p.: 45.5-46°C. (lit.[54] 46-47°C.).

9.  **Para-fluoro-β-nitrostyrene.**-- This synthesis was carried out on a 0.20 mole scale. The crude product was recrystallized from a minimum amount of warm 95 percent ethanol. The product was filtered and dried under vacuum at room temperature for 24 hrs. The yield was 15.2 g. (45 percent) of yellow needles, m.p.: 100-101°C. (lit.[54] 100-101°C.).

10.  **Ortho-chloro-β-nitrostyrene.**-- This synthesis was carried out on a 0.25 mole scale. The crude product was recrystallized from a minimum amount of 95 percent ethanol. The yield was 26.5 g. (57.6 percent yield) of long yellow needles, m.p.: 46.5-47.5°C. (lit.[21] 47-47.5°C.).

11.  **Para-chloro-β-nitrostyrene.**-- This synthesis was carried out on a 0.10 mole scale by the previously described method. The crude

product was dissolved in 200 mls. of warm ethanol, filtered, and to this was added 75 mls. of deionized water. The solution was then chilled to -15°C. for 24 hrs. The yield was 11.5 g. (62.5 percent yield) of yellow needles, m.p.: 113-114°C. (lit.[55] 113-114°C.).

12. <u>Ortho-bromo-β-nitrostyrene</u>.-- This synthesis was carried out on a 0.14 mole scale by the previously described modified Thiele reaction. The crude product was dissolved in 125 mls. of warm 95 percent ethanol, filtered, and chilled to -15°C. for 24 hrs. yielding 15.80 g. (49.5 percent yield) of yellow needles, m.p.: 86-86.5°C. (lit.[22] 84°C.).

13. <u>Meta-bromo-β-nitrostyrene</u>.-- This synthesis was carried out on a 0.14 mole scale by the same method. The crude product was again dissolved in a minimum amount of hot 95 percent ethanol (175 mls.) and chilled to -15°C. for 24 hrs. The long yellow needles were filtered and dried under vacuum at room temperature for 24 hrs. The yield was 14.49 g. (45.4 percent yield) of product, m.p.: 60-61°C. (lit.[56] 59-60°C.).

14. <u>Para-bromo-β-nitrostyrene</u>.-- This monomer was synthesized on a 0.134 mole scale. The crude product was dissolved in 75 mls. of THF and to this was added 100 mls. of 95 percent ethanol. The resulting solution was chilled to -15°C. for 24 hrs. The resulting crystals were filtered and dried under vacuum at room temperature for 24 hrs. The yield was 9.93 g. (32.5 percent yield) of purified product, m.p.: 148.5-149°C. (lit.[57] 175°C.). Subsequent recrystallizations failed to change the melting point. Due to this discrepancy in melting points, the compound was analyzed in greater detail.

The nmr spectrum of the compound was comprised of a 2-proton

AB quartet for the nitrovinyl group, $\tau H_A = 2.01$, $\tau H_B = 2.45$ ($J_{AB} = 14$ hz.); and a 4-proton $A_2B_2$ quartet for the aromatic protons, $\tau H_A = 2.37$, $\tau H_B = 2.58$ ($J_{AB} = 9$ hz.). The infra-red spectrum included strong sharp absorptions at $1628$ $cm^{-1}$ ($\nu$ C=C of nitrovinyl group) and $1580$ $cm^{-1}$ ($\nu$ C=C of aromatic nucleus).

Analysis: Calculated for $C_8H_6NO_2Br$, Mwt. 228.05, percent: C, 42.13; H, 2.65; N, 6.14; Br, 35.04. Found, percent: C, 42.40; H, 2.59; N, 6.20; Br, 35.26.

15. Meta-nitro-β-nitrostyrene.-- This monomer was synthesized on a 0.25 mole scale by the previously described method. The crude product was dissolved in a minimum amount of warm 95 percent ethanol, filtered, and chilled to $-15^\circ$C. for 24 hrs. yielding 13.7 g. (28.3 percent yield) of product, m.p.: $121.5-122.5^\circ$C. (lit.[58] $122-124^\circ$C.).

16. Para-nitro-β-nitrostyrene.-- This synthesis was carried out on a 0.10 mole scale by the previously described method. The crude product was dissolved in a minimum amount of acetone, diluted with 95 percent ethanol, and recrystallized out with water. This method yielded 3.7 g. (19 percent yield) of product, m.p.: $204-205^\circ$C. (lit.[59] $199-200^\circ$C.).

B. Determination of the Rate of Propagation in the Anionic Polymerization of Certain Meta- and Para-substituted β-nitrostyrenes and β-nitrostyrene

Essentially, the same procedure was used in the study of each monomer so, to avoid repetition, the procedure will be described only once in its entirety. Variations, when deemed necessary, will be described.

1. β-nitrostyrene.-- 10.00 mmole quantities (1.490 g.) of the monomer were weighed out to the nearest mg. in 60 ml. weighing

bottles which had been scrupulously washed, rinsed with acetone, and oven dried at $110^{\circ}$C. Each sample was dissolved and diluted to 40.0 mls. (0.250 M.) in a solvent mixture prepared by mixing 2 parts by volume of absolute ethanol with 1 part of purified[60] THF. The solutions were then equipped with magnetic stirrers and Teflon-covered magnets and placed in a thermostatted ($28^{\circ} \pm 0.1^{\circ}$C.) bath and allowed to come to thermal equilibrium. Stirring speed was maintained at a moderate rate to minimize conversion of mechanical energy to thermal energy. Using a 0.25 ml. tuberculin syringe, 0.20 ml. of sodium ethoxide/ethanol (0.105 mmole/ml.) was injected at time $t = 0$, giving an initiator concentration of $5.25 \times 10^{-4}$ M. At time (t), 0.5 ml. of 1 M. sulfuric acid in ethanol was injected to terminate polymerization. The resulting precipitated polymer was then centrifuged in carefully washed pre-weighed centrifuge tubes, washed once with methanol, recentrifuged, and dried under vacuum (0.025 mm Hg) for 12 hrs. at room temperature. The product was then weighed to the nearest tenth milligram.

Polymer yields were plotted in terms of moles of monomer units/ liter of solution converted to polymer. The slope of that line gives the observed rate of polymerization $\nu_p$, expressed as moles/liter/sec. The rate constant, $k_p$, was then calculated using the expression $\nu_p = k_p[M][M^-]$, where $[M^-]$ is assumed to be equal to initiator concentration $[I]$.

2. Meta,$\beta$-dinitrostyrene.-- Due to the limited solubility of this compound in the chosen solvent system, only 5.00 mmole samples (0.970 g.) of the monomer were polymerized. In all other respects, this experiment was carried out in a manner identical to that for $\beta$-nitrostyrene.

3. <u>Para,β-dinitrostyrene</u>.-- Due to the relatively low polarity of this compound in this solvent system, its solubility was quite limited. As a result, 5 mmole samples of the monomer (0.970 g.) were dissolved in 140 mls. of solvent. Initial initiator concentrations were $5.25 \times 10^{-4}$ M. as before.

Other monomers were polymerized either on a 5.00 mmole or 10.00 mmole scale depending upon the availability of the monomer as well as its molecular weight. The data from these experiments is tabulated in Table 1 and plotted in Figures 9-18, pages 78 through 87. The calculated propagation rate constants ($k_p$) appear in Table 10, page 88.

C. <u>Determination of the Rate of Initiation of Two Representative Monomers, Para-methoxy-β-nitrostyrene and β-nitrostyrene</u>

The rate of reaction of sodium ethoxide with monomer was determined in the following manner. A solution of para-methoxy-β-nitrostyrene in the usual solvent system (33 volume percent THF in absolute ethanol) was prepared with a concentration of $3 \times 10^{-5}$ M. and 3.9 mls. of the solution were placed in a thermostatted ($25 \pm 0.1^{\circ}$C.) quartz cell in the ultra-violet spectrophotometer under a $N_2$ purge. The reaction was monitored by measuring the absorbance at the monomer's absorption maximum at $\lambda_{max.}$ = 348 mμ ($\varepsilon$ = 20,600). At time t = 0, 0.1 ml. of sodium ethoxide in absolute ethanol ($5 \times 10^{-2}$ M.) was injected rapidly with a tuberculin syringe (0.25 ml.). The resulting solution, containing about a 10-fold excess of initiator ($5 \times 10^{-4}$ M.) was quickly stirred and the progress of reaction followed by watching the steady decrease in absorbance. Readings were taken every 10 seconds. The

TABLE 1

Kinetic Data of Propagation Reactions

$[\text{NaOEt}] = 5.25 \times 10^{-4}$ M.

| Monomer | Run | Monomer Feed (g.) | Monomer Conc. (M.) | Time (sec.) | Poly. Yield (mg.) | Percent Conv. |
|---|---|---|---|---|---|---|
| (A.) β-nitrostyrene | 1 | 1.492 | 0.250 | 30 | 21.5 | 1.44 |
| | 2 | 1.492 | 0.250 | 60 | 42.0 | 2.82 |
| | 3 | 1.491 | 0.250 | 90 | 61.5 | 4.12 |
| | 4 | 1.491 | 0.250 | 120 | 75.0 | 5.03 |
| | 5 | 1.490 | 0.250 | 150 | 81.0 | 5.44 |
| | 6 | 1.490 | 0.250 | 180 | 90.0 | 6.04 |
| (B.) meta-methyl-β-nitrostyrene | 1 | 1.634 | 0.250 | 30 | 10.8 | 0.66 |
| | 2 | 1.630 | 0.250 | 45 | 22.8 | 1.40 |
| | 3 | 1.626 | 0.250 | 60 | 28.4 | 1.75 |
| | 4 | 1.630 | 0.250 | 75 | 37.6 | 2.30 |
| (C.) para-methyl-β-nitrostyrene | 1 | 1.630 | 0.250 | 33 | 15.5 | 0.95 |
| | 2 | 1.632 | 0.250 | 46 | 25.0 | 1.53 |
| | 3 | 1.630 | 0.250 | 60 | 33.0 | 2.02 |
| | 4 | 1.630 | 0.250 | 75 | 46.5 | 2.84 |
| (D.) meta-methoxy-β-nitrostyrene (trial 1) | 1 | 0.895 | 0.125 | 30 | 14.9 | 1.66 |
| | 2 | 0.895 | 0.125 | 45 | 25.7 | 2.87 |
| | 3 | 0.895 | 0.125 | 60 | 38.3 | 4.27 |
| | 4 | 0.895 | 0.125 | 75 | 53.4 | 5.95 |

TABLE 1   continued

| Monomer | Run | Monomer Feed (g.) | Monomer Conc. (M.) | Time (sec.) | Poly. Yield (mg.) | Percent Conv. |
|---|---|---|---|---|---|---|
| (D.) meta-methoxy-β- nitrostyrene (trial 2) | 1 | 0.895 | 0.125 | 30 | 13.4 | 1.50 |
| | 2 | 0.895 | 0.125 | 45 | 24.8 | 2.88 |
| | 3 | 0.895 | 0.125 | 60 | 38.2 | 4.27 |
| | 4 | 0.895 | 0.125 | 75 | 47.5 | 5.30 |
| (E.) para-methoxy-β- nitrostyrene (trial 1) | 1 | 1.790 | 0.250 | 30 | 7.0 | 0.391 |
| | 2 | 1.790 | 0.250 | 45 | 13.5 | 0.755 |
| | 3 | 1.790 | 0.250 | 60 | 19.1 | 1.06 |
| | 4 | 1.792 | 0.250 | 75 | 34.2 | 1.90 |
| (Trial 2) | 1 | 1.790 | 0.250 | 30 | 9.0 | 0.502 |
| | 2 | 1.790 | 0.250 | 75 | 17.5 | 0.978 |
| | 3 | 1.790 | 0.250 | 60 | 22.1 | 1.23 |
| | 4 | 1.790 | 0.250 | 90 | 31.0 | 1.73 |
| (F.) para-fluoro-β- nitrostyrene | 1 | 1.670 | 0.250 | 30 | 36.3 | 2.18 |
| | 2 | 1.673 | 0.250 | 45 | 50.2 | 3.00 |
| | 3 | 1.671 | 0.250 | 60 | 63.6 | 3.80 |
| | 4 | 1.670 | 0.250 | 75 | 72.4 | 4.33 |
| (G.) para-chloro-β- nitrostyrene | 1 | 0.917 | 0.125 | 30 | 11 | 1.20 |
| | 2 | 0.919 | 0.125 | 60 | 21 | 2.29 |
| | 3 | 0.918 | 0.125 | 93 | 28 | 3.05 |
| | 4 | 0.918 | 0.125 | 120 | 33 | 3.60 |
| | 5 | 0.917 | 0.125 | 150 | 33 | 3.60 |
| | 6 | 0.917 | 0.917 | 180 | 35 | 3.82 |

TABLE 1   continued

| Monomer | Run | Monomer Feed (g.) | Monomer Conc. (M.) | Time (sec.) | Poly. Yield (mg.) | Percent Conv. |
|---------|-----|-------------------|--------------------|-------------|--------------------|---------------|
| (H.) meta-bromo-β-nitrostyrene | 1 | 1.140 | 0.125 | 31 | 32.6 | 2.86 |
| | 2 | 1.141 | 0.125 | 45 | 48.6 | 4.25 |
| | 3 | 1.140 | 0.125 | 60 | 64.2 | 5.62 |
| | 4 | 1.140 | 0.125 | 90 | 73.9 | 6.48 |
| (I.) para-bromo-β-nitrostyrene | 1 | 1.140 | 0.125 | 30 | 25.2 | 2.24 |
| | 2 | 1.140 | 0.125 | 46 | 37.6 | 3.40 |
| | 3 | 1.140 | 0.125 | 60 | 47.4 | 4.15 |
| | 4 | 1.141 | 0.125 | 75 | 56.5 | 4.95 |
| (J.) meta,β-dinitrostyrene (Trial 1) | 1 | 0.970 | 0.125 | 10 | 13.1 | 1.35 |
| | 2 | 0.970 | 0.125 | 15 | 17.5 | 1.81 |
| | 3 | 0.970 | 0.125 | 20 | 20.0 | 2.03 |
| | 4 | 0.970 | 0.125 | 30 | 24.5 | 2.53 |
| (Trail 2) | 1 | 0.970 | 0.125 | 15 | 15.9 | 1.64 |
| | 2 | 0.970 | 0.125 | 30 | 21.9 | 2.26 |
| | 3 | 0.970 | 0.125 | 45 | 29.0 | 2.99 |
| (K.) para,β-dinitrostyrene | 1 | 0.970 | 0.0357 | 30 | 10.9 | 1.12 |
| | 2 | 0.970 | 0.0357 | 60 | 13.3 | 1.38 |
| | 3 | 0.970 | 0.0357 | 90 | 18.2 | 1.87 |

rate constant was determined by plotting $\log (OD_t - OD_\infty)/[I]$ vs. t where I is the initiator concentration.[61] The slope of the resulting plot is $-k_i$, the rate constant of initiation. The plot appears in Figure 6, page 74. The rate constant thus determined was $k_i$ = 2.86 1. mole$^{-1}$ sec.$^{-1}$ The rate constant of initiation for β-nitrostyrene was carried out in the same manner. The rate of reaction was obtained by monitoring the absorption maximum at 309 mμ (ε = 12,000). This reaction was also run under $N_2$. Due to the lower ε for this monomer, a monomer concentration of 5 x 10$^{-5}$ M. was used. The initiator concentration was again 5 x 10$^{-4}$ M. The plot of data appears in Figure 7, page 75. The rate constant obtained was $k_i$ = 3.51 1. mole$^{-1}$ sec.$^{-1}$

D. Effect of Changes in Initiator Concentration on the Rate of Anionic Polymerization of β-nitrostyrene

10 mmole quantities of β-nitrostyrene, which had been freshly prepared and recrystallized, were weighed out into the 60 ml. flasks and diluted to 40 ml. with the usual 33 percent THF in ethanol.

The solutions were allowed to come to equilibrium with stirring in the 28°C. bath. To each was added a varied amount of the initiator solution via a 0.25 ml. syringe. Each was allowed to polymerize for 30 sec. before termination. After termination with 0.5 mmole of hydrochloric acid, the polymer was centrifuged, washed with methanol, and dried under vacuum and weighed to the nearest 0.1 mg. A plot of this data appears in Figure 19, page 90.

TABLE 2

Kinetic Data for Changing Initiator Concentration

| Vol. of Initiator (ml.) | Conc. of Initiator $M \times 10^4$ | Polymer Yield (mg.) | Percent Conv. |
|---|---|---|---|
| 0.05 | 1.01 | 3.9 | 0.26 |
| 0.10 | 2.02 | 8.5 | 0.57 |
| 0.15 | 3.03 | 12.3 | 0.82 |
| 0.20 | 4.05 | 16.7 | 1.12 |
| 0.25 | 5.06 | 21.6 | 1.45 |
| 0.30 | 6.07 | 29.3 | 1.97 |

E. Determination of the Molecular Weight Distribution Curves of Some
   Representative Monosubstituted Poly-β-nitrostyrenes

The molecular weight distribution curves of some of the DMF

soluble polymers obtained during the rate of propagation study were

determined by gel permeation chromatographic (GPC) analysis. 1 wt.

percent solutions of the polymer (3 mls.) were prepared by dissolving

the finely ground polymer in DMF either at room temperature of at $110^{o}C$.

depending upon the apparent solubility. The resulting solutions were

filtered through medium porosity sintered glass filtering crucibles

and then chromatographed on the GPC. Two typical molecular weight

distribution curves appear in Figures 7 and 8, pages 75 and 76. Using

the laborious method described in the instrument literature, the number

average molecular length, $\overline{A}_n$, and weight average molecular length, $\overline{A}_w$,

(both in angstroms) were calculated. Using a calibration curve derived

from polystyrene standard samples, values for the number and weight

average molecular weights ($\bar{M}_n$ and $\bar{M}_w$, respectively) were determined.
The results of these determinations are tabulated in Table 5, page 62.
It should be noted that poly-para-methoxy-$\beta$-nitrostyrene and poly-$\beta$-
nitrostyrene were found to not dissolve completely, even when heated
to $110^\circ$C. Butler[5] reported depolymerization of poly-$\beta$-nitrostyrene
under such conditions. Although depolymerization was not proven in
the present work, it was probably occurring in the case of these two
polymers.

F.  The Role and Mechanism of Initiation and Termination in the Anionic
    Polymerization of Meta and Para,$\beta$-dinitrostyrene

    1.  Polymerization of para,$\beta$-dinitrostyrene.-- 1.94 g. of
monomer were dissolved in 150 mls. of 33 percent THF in absolute ethanol
and reacted with 5 mole percent sodium ethoxide.  The addition of ini-
tiator resulted in the formation of a deep red solution which slowly
changed to a very dark amber color.  The polymerization was carried
out over a 24-hr. period.  The dark amber mixture was then acidified
and centrifuged.  The yellow precipitated product was washed with
methanol, recentrifuged, and dried under vacuum at room temperature
yielding 0.10 g. (5.2 percent conversion) of light amber amorphous
solid, $T_m$: 295-300$^\circ$C. (dec.).  Insufficient yield was obtained for an
intrinsic viscosity determination.

        The infra-red spectrum of the product included a strong absorp-
tion at 1350 cm$^{-1}$ conjugated nitro; strong 1525 cm$^{-1}$ nitro; weak 1600
cm$^{-1}$ $\nu$ C=C aromatic; medium 1100 cm$^{-1}$ $\nu$ C-O of aliphatic ether.  The
strong 1635 cm$^{-1}$ ($\nu$ C-O of nitrovinyl) was not detectable and there was
no indication of any significant absorption between 1200 and 1250 cm$^{-1}$
($\nu$ C-O of aromatic ether).

2.   <u>Polymerization of meta,β-dinitrostyrene.</u>-- This reaction
was carried out as described for the para isomer except only 50 mls. of
solvent were used.  0.430 g. (22 percent conversion) of a light amber
glass-like solid was obtained, $T_m$: 290-295°C. (dec.), $[\eta]$ = 0.11 dl/g.
in DMSO.

When this polymerization was carried out in pure THF, only
0.181 g. (9.3 percent conversion) was obtained, $[\eta]$ = 0.06 dl/g. in
DMSO.

The infra-red spectra of the two products were identical and
included strong absorptions at 1375 cm$^{-1}$ and 1450 cm,$^{-1}$ nitro groups;
medium at 1560 cm,$^{-1}$ ν C=C aromatic; weak at 1100 cm,$^{-1}$ ν C-O aliphatic
ether linkage.  Again, there was no indication of an aromatic ether.

3.   <u>The reaction of sodio-malonic ester with para,β-dinitro-
styrene and determination of the structure of the product.</u>-- The
method of Perckalin and Sopova[62] was used to carry out this reaction.
1.30 g. of para-β-dinitrostyrene (0.0067 mole) suspended in 200 mls.
of dry methanol at room temperature was added to the reaction mixture
of 1.43 g. (0.00837 mole) diethyl malonic ester, 0.186 g. of sodium
(0.0081 mole), and 15 mls. of methanol at room temperature.  The mono-
mer quickly dissolved forming a gradually darkening amber solution.
The red color, characteristic of the reaction of sodium ethoxide with
this compound, was not present.  The solution was then heated to 45°C.
and kept at this temperature (± 5°C.) for two hours.  The dark amber
solution was then chilled in ice water and acidified with glacial ace-
tic acid (50 mls.) followed by addition of 25 mls. of concentrated hydro-
chloric acid.  The product was then extracted with ether and the ether
removed by distillation.

The product was not isolated in pure form although the nmr
spectrum of the crude product, which included a 4-proton $A_2B_2$ quartet
at $\tau H_A$ = 2.70, $\tau H_B$ = 3.11 ($J_{AB}$ = 9 hz.); a 2-proton doublet at $\tau$ = 4.93;
a 2-proton multiplet at $\tau$ = 5.5-6.2; and a 6-proton doublet at $\tau$ = 6.25,
indicated a fair degree of purity.

This nmr spectrum indicates that a 1:1 adduct was obtained.
However, it does not distinguish between carbanion attack on the $\alpha$-
carbon as opposed to attack on the $\beta$-carbon. Apparently, trans-esteri-
fication occurred between the ethyl ester and solvent as indicated by
the methoxy singlets.

The crude product was placed in a 100 ml. round-bottom flask
with 35 mls. of concentrated hydrochloric acid. The resulting mixture
was refluxed for 24 hrs. The mixture was then placed in a separatory
funnel while still hot and the bottom layer was separated into another
separatory funnel. Upon cooling to room temperature, 0.122 g. of
amber crystalline solid (m.p.: 118-119°C.) formed on the sides of the
separatory funnel.

The aqueous solution was found to be soluble in ether due to
the high acid content. The acid was then partially neutralized with
aqueous potassium hydroxide and the product was then extracted with
ether. Distillation of the ether under vacuum yielded 1.09 g. of amber
solid contaminated with an amber oil. The solid was placed in a sin-
tered glass filtering crucible and washed with benzene. This effectively
removed the oil and the resulting light amber powder was dried in a
110°C. over for 24 hrs.

The nmr spectrum (acetone-d6) of the compound, when compared
with Sadtler spectrum number 6595 (phenylsuccinic acid), conclusively

identified the structure of this product as para-nitrophenylsuccinic

acid. The spectrum included a 4-proton $A_2B_2$ quartet for the aromatic

protons, $\tau H_A = 1.75$, $\tau H_B = 2.33$ ($J_{AB} = 9$ hz.); a one-proton ABC quartet

for the benzylic proton, $\tau H_A = 5.70$ ($J_{AB} = 9$ hz., $J_{AC} = 6$ hz.); and 2

one-proton ABC quartets for the non-equivalent methylene protons $\tau H_B = $

6.83, $\tau H_C = 7.33$ ($J_{gem} = 17$ hz.).

The infra-red spectrum (KBr pellet) of the product included

a broad absorption between 3500 and 2500 cm;$^{-1}$ ($\nu$ O-H of a hydrogen

bonded carboxyl group) strong absorption at 1710 cm$^{-1}$ ($\nu$ C=O); and a

medium absorption at 1600 cm$^{-1}$ ($\nu$ C=C aromatic).

The melting point of the compound (218-218.5$^{\circ}$C.) agreed well

with that reported[63] for para-nitrophenylsuccinic acid and the spectral

data supported that assignment.

The total yield was 1.21 g. (75 percent yield).

4. Reaction of sodio-malonic ester with meta,β-dinitrostyrene

and determination of the structure of the product.-- This reaction

was carried out in an identical manner as that previously described

for the para isomer. The reaction was carried out using 1.93 g.

(0.0102 mole) of meta,β-dinitrostyrene, 2.04 g. of malonic ester, and

0.284 g. of sodium metal.

The nmr spectrum of the aliphatic protons of the crude product

was essentially identical to that of the previously described malonic

ester derivative.

This crude product was treated with concentrated hydrochloric

acid as before. 0.107 g. of light amber crystals (m.p.: 106-109$^{\circ}$C.)

formed when the aqueous layer of the reaction mixture cooled to room

temperature.

Work-up of the remaining product yielded 1.839 g. of very light amber powder, m.p.: 217-219°C.

The infra-red spectrum of the product included a strong broad absorption at 2400-3400 cm$^{-1}$ ($\nu$ O-H hydrogen bonded); a strong sharp absorption at 1705 cm$^{-1}$ ($\nu$ C=O); a strong absorption at 1540 cm$^{-1}$ ($\nu$ nitro group); and a weak absorption at 1580 cm$^{-1}$ ($\nu$ C=C aromatic).

The nmr spectrum of the aliphatic protons was essentially identical to that of the corresponding para-substituted compound.

Although the melting point of this compound was higher than the literature value[64] of the melting point of meta-nitrophenylsuccinic acid (204°C.), the spectral data indicates that its structure is analogous to that of para-nitrophenylsuccinic acid. The elemental analysis was in close agreement with the theoretical values for meta-nitrophenyl-succinic acid.

5. <u>The relative acidity of poly-meta,β-dinitrostyrene</u>.--
This question was first tested qualitatively by dissolving a small sample (about 20 mg.) of the polymer in about 10 mls. of dimethylsul-foxide (DMSO). A couple of drops of 1 M. sodium ethoxide, when added to the very light amber solution, produced a very dark amber solution. This observation prompted a spectroscopic study of the reaction.

A solution of polymer in DMSO of concentration 1.6 x 10$^{-4}$ moles/1. (in terms of monomer units) was prepared. It was found to be transparent from 400-850 mμ. Addition of sufficient sodium ethoxide to give a concentration of 10$^{-3}$ M. produced an absorption maximum at about $\lambda_{max.}$ = 490 mμ, A = 0.30.

The following experiment was carried out to determine the reactivity toward monomer of this apparent new species of anion being

formed. A solution of 0.112 g. of poly-meta,β-dinitrostyrene in 10

mls. of DMSO (dried over 4Å molecular sieves for 24 hrs.) was reacted

with 0.2 ml. of 0.5 M. sodium ethoxide in DMSO for 12 hrs. under $N_2$.

0.75 g. of para-bromo-β-nitrostyrene, dissolved in 10 mls. of DMSO, was

then added to the dark amber solution.

A blank containing 10 mls. of DMSO and 0.2 ml. of the sodium

ethoxide solution had been prepared and left standing under $N_2$ for 12

hrs. 0.75 g. of para-bromo-β-nitrostyrene in DMSO was also added to

the blank. At the end of 20 minutes' reaction time with the monomer,

each reaction was terminated with 1 M. HCl in methanol and added to 100

mls. of vigorously stirred methanol. The solution containing the poly-

meta,β-dinitrostyrene yielded no polymer. The blank yielded 0.36 g.

of poly-para-bromo-β-nitrostyrene (48 percent conversion).

6. The relative acidity of poly-para,β-dinitrostyrene.-- A

solution of the polymer ($1 \times 10^{-4}$ M. in monomer units) in dry DMSO was

prepared. The visible spectrum of the solution was free of absorption

maxima. To this solution was added sodium ethoxide ($3 \times 10^{-4}$ M.).

The resulting amber solution gave an absorption at $\lambda_{max.}$ = 433 mμ,

A = 0.15.

Another polymer solution ($2 \times 10^{-4}$ M. in monomer units) in

DMSO was prepared containing $1.5 \times 10^{-5}$ M. sodium ethoxide. This solu-

tion was allowed to react for 24 hrs. to reach equilibrium. A solution

of para-methoxy-β-nitrostyrene ($4 \times 10^{-5}$ M.) in DMSO was also prepared.

The planned procedure was to mix the two solutions and monitor the reac-

tion by watching the 348 mμ absorption maximum of para-methoxy-β-nitro-

styrene which was already known to disappear upon reaction. The absor-

bance of the initial polymer/initiator solution at 348 mμ was A = 0.40.

Another polymer solution ($2 \times 10^{-4}$ M. in monomer units) in DMSO was prepared containing $1.5 \times 10^{-5}$ M. sodium ethoxide. This solution was allowed to react for 24 hrs. to reach equilibrium. A solution of para-methoxy-$\beta$-nitrostyrene ($4 \times 10^{-5}$ M.) in DMSO was also prepared. The planned procedure was to mix the two solutions and monitor the reaction by watching the 348 m absorption maximum of para-methoxy-$\beta$-nitrostyrene which was already known to disappear upon reaction. The absorbance of the initial polymer/initiator solution at 348 m$\mu$ was A = 0.05 while that of the initial monomer solution was A = 0.77. Equal amounts of the two solutions were mixed and the initial absorbance of the solution was A = 0.40. This did not change over a period of one hour. The expected theoretical value for no reaction would have been 0.41.

7. <u>The reaction between meta,$\beta$-dinitrostyrene and sodium ethoxide</u>.-- A solution of meta,$\beta$-dinitrostyrene ($6.6 \times 10^{-4}$ M.) was prepared in DMSO. Sufficient 1 M. sodium ethoxide, in absolute ethanol, was added to the solution to make it $4 \times 10^{-3}$ M. in that compound. The resulting bright green solution possessed an absorption maximum at $\lambda_{max.}$ = 657 m$\mu$, A = 0.77.

When a solution of meta,$\beta$-dinitrostyrene in DMSO ($1 \times 10^{-3}$ M.) was reacted with a less than equipolar amount of sodium ethoxide ($1 \times 10^{-4}$ M.) the 657 m$\mu$ peak was initially fairly strong but decreased fairly rapidly over a period of 3 minutes. As it decreased, a new but weaker absorption maximum appeared at about 490 m$\mu$.

8. <u>The reaction of para,$\beta$-dinitrostyrene with sodium ethoxide</u>.-- A solution of para,$\beta$-dinitrostyrene ($5 \times 10^{-3}$ M.) in DMSO containing an excess of sodium ethoxide ($1.5 \times 10^{-2}$ M.) gave an absorption maximum at $\lambda_{max.}$ = 539 m$\mu$, A = 0.46. This value did not change appreciably over a 10-minute period.

When a solution of the same monomer and same concentration was reacted with sodium ethoxide in a less than equimolar quantity ($1 \times 10^{-4}$ M.), an absorption maximum was again observed at 539 mµ. However, the absorbance steadily decreased over a one hour period. No other absorption maximum could be observed in the visible region. If there was a weak absorption at 433 mµ, it was obscured by the overlapping tail of a strong absorption in the ultra-violet region, $\lambda_{max.}$ = 293 mµ.

## Studies of Certain Aspects of the Ortho-effect

1. Effect of initiator species on polymerization of certain monomers.-- Anionic polymerizations of several ortho, meta, and para-substituted β-nitrostyrenes were carried out on 6 mmole scales with different initiators (3 mole percent) to determine the effect of the size of the initiating ion on the extent of polymerization. Polymerizations utilizing hydroxide and ethoxide as initiators were carried out in 30 mls. of absolute ethanol while those utilizing t-butoxide were carried out in 50 mls. of absolute t-butanol. Unless otherwise stated, all polymerizations were carried out over 24-hour periods at room temperature with magnetic stirring. No attempts were made to exclude air from the reaction mixtures.

The precipitated polymers were filtered out in pre-weighed sintered glass filtering crucibles (medium porosity), washed once with methanol and dried under vacuum at room temperature for 24 hrs. The results are tabulated in Table 3, page 50.

2. Determination of the rate of polymerization of certain ortho-substituted β-nitrostyrenes.-- The data in Table 3 prompted a quantitative investigation of the rate of polymerization of different

TABLE 3

The Effect of Initiator Ion on Polymer Yields

| β-nitrostyrene | Initiator | Feed (g.) | Yield (g.) | Percent Conv. |
|---|---|---|---|---|
| ortho-fluoro | NaOH | 1.007 | 0.263 | 26.1 |
| | NaOEt | 1.004 | 0.264 | 26.3 |
| | NaOtBu | 1.006 | 0.216 | 21.5 |
| | NaOEt* | 1.004 | 0.092 | 9.16 |
| meta-fluoro | NaOH | 1.002 | 0.803 | 80.1 |
| | NaOEt | 1.001 | 0.752 | 75.2 |
| | NaOtBu. | 1.000 | 0.837 | 83.7 |
| | Na)Et* | 1.010 | 0.424 | 42.0 |
| para-fluoro | NaOH | 1.002 | 0.913 | 90.1 |
| | NaOEt | 1.001 | 0.905 | 90.5 |
| | NaOtBu | 1.013 | 0.903 | 89.7 |
| | NaOEt* | 1.002 | 0.643 | 64.2 |
| ortho-methoxy | NaOH | 1.072 | 0.000 | 0.0 |
| | NaOEt | 1.074 | 0.000 | 0.0 |
| | NaOtBu | 1.074 | 0.008 | 0.75 |
| meta-methoxy | NaOH | 1.079 | 1.016 | 94.0 |
| | NaOEt | 1.074 | 1.003 | 95.8 |
| | NaOtBu | 1.074 | 0.872 | 81.0 |

*Polymerization time 1 hr., all others 24 hrs.

TABLE 3 continued

| β-nitrostyrene | Initiator | Feed (g.) | Yield (g.) | Percent Conv. |
|---|---|---|---|---|
| para-methoxy | NaOH | 1.074 | 1.029 | 95.6 |
| | NaOEt | 1.074 | 1.018 | 94.8 |
| | NaOtBu | 1.074 | 0.893 | 83.5 |
| ortho-(2-vinyloxy)ethoxy | NaOH | 1.413 | 0.009 | 0.70 |
| | NaOEt | 1.418 | 0.010 | 0.71 |
| | NaOtBu | 1.411 | 0.025 | 1.77 |

ortho-substituted β-nitrostyrenes. In addition to the ortho-fluoro com-
pound, ortho-chloro and ortho-bromo-β-nitrostyrene were also synthesized.
These experiments were carried out using the same general procedure as
was used in the kinetic study of the meta and para-substituted compounds.

A stock solution of initiator was prepared by dissolving 2.3 g.
of metallic sodium in 100 mls. of absolute ethanol in a 250 ml. erlen-
meyer flask covered with a septum. The septum was vented with a syringe
needle and purged with dried nitrogen during and after the reaction.
The initiator solution was then standardized against potassium acid
phthalate (concentration thus obtained = 1.05 M.).

Because of the expected slowness of these polymerizations, two
mole percent initiator was used. 10 mmole quantities of monomer were
dissolved in 33 percent THF (by volume) in absolute ethanol and diluted
to 40.0 mls. (0.250 M.). At time t = 0, 0.20 ml. of the stock initiator
solution was injected into each monomer solution and the polymerization
then terminated at time t by acidification. The results appear in
Table 4. A plot of polymer yield [P] expressed in terms of moles of
monomer units per liter versus time appears in Figure 25, page 104.

TABLE 4

Kinetic Data of the Anionic Polymerization of
Ortho-fluoro-β-nitrostyrene

| Feed (g.) | Polymerization Time (sec.) | Polymer Yield (mg.) | Percent Conv. |
|---|---|---|---|
| 1.670 | 83 | 34.6 | 2.07 |
| 1.670 | 100 | 41.5 | 2.48 |
| 1.671 | 65 | 26.5 | 1.58 |
| 1.671 | 120 | 49.4 | 2.96 |

3. <u>The reaction of ortho-substituted β-nitrostyrenes with excess sodium ethoxide.</u>-- These qualitative experiments were carried out in an effort to determine whether the ortho-effect, as manifested in the previous experiments, is the primary result of an inhibition of initiation or propagation or both.

A solution of 3 mmoles of each of the following compounds was prepared in 8 mls. of 33 percent THF in ethanol; ortho-fluoro, ortho-chloro, ortho-bromo, ortho-methoxy, and ortho-(2-vinyloxy)ethoxy-β-nitrostyrene. The nmr spectrum of each solution was recorded with special attention devoted to the nitrovinyl proton-aromatic proton region. 5 mls. of the 1.05 M. sodium ethoxide solution were then injected rapidly into the monomer solutions. The nmr spectrum of the resulting solution was then taken as rapidly as possible (approximately 30 sec. after injection). These spectra appear in Figures 26 through 30. It can be readily seen in each spectrum that the AB quartet (nitrovinyl protons) is not detectable after 30 seconds.

## Instruments Used

A Beckman DK-2A double-beam recording spectrophotometer was used to obtain all ultra-violet and visible spectra.

Beckman IR-8 and IR-10 infra-red spectrophotometers were used to obtain all infra-red spectra.

A Varian A-60 nmr spectrometer was used to obtain all nmr spectra and unless otherwise indicated, all spectra were obtained using deuterated chloroform ($CDCl_3$) as the solvent.

A Waters GPC 300 gel permeation chromatograph was used with calibrated polystyrene gel columns to obtain all molecular weight distribution data.

A Thomas Hoover Capillary Melting Point Apparatus was used to obtain the melting points of all monomeric compounds and the melting points reported are uncorrected.

A Fisher Johns melting point apparatus was used to obtain the melting points of all polymeric materials.

A Vacuum/Atmospheres Corporation Dri-Lab was used for all inert atmosphere work.

## Source and Methods of Purification of Reagents

Ortho, meta, and para-fluoro-benzaldehydes (reagent) were obtained from PCR and used without further purification.

Ortho-chloro-benzaldehyde (reagent) was obtained from Fisher and used without purification.

Para-chloro-benzaldehyde (reagent) was obtained from Aldrich and used without further purification.

Ortho, meta, and para-bromo-benzaldehydes (reagent) were obtained from PCR and used without further purification.

Ortho, meta, and para-anisaldehydes (practical) were obtained from Aldrich and used without further purification.

Meta-tolualdehyde (practical) was obtained from Aldrich and used without further purification.

Para-tolualdehyde (practical) was obtained from Fisher and used without further purification.

Para-nitro-benzaldehyde (practical) was obtained from Fisher and recrystallized from ethanol and water.

Meta-nitro-$\beta$-nitrostyrene (practical) was obtained from Aldrich and recrystallized from ethanol and water.

Benzaldehyde (practical) was obtained from Fisher and used without purification.

Salicylaldehyde (practical) was obtained from Fisher and used without purification.

Para-hydroxy-benzaldehyde (practical) was obtained from Fisher and used directly.

Meta-hydroxy-benzaldehyde (practical) was obtained from Aldrich and used without further purification.

Para-nitro-phenol (practical) was obtained from Fisher and used without purification.

β-chloroethyl vinyl ether (practical) was obtained from Fisher and purified by distillation under vacuum.

# CHAPTER III

## RESULTS AND DISCUSSION

### Synthesis and Chemistry of Ortho, Meta, and Para-(2-vinyloxy)ethoxy-β-nitrostyrenes

## A. Preparation of the Monomers

1. Synthesis of ortho and para-(2-vinyloxy)ethoxy-β-nitro-styrenes.-- The method of Thompson was modified by lowering the reaction temperature of the Thiele reaction to $-5°C$. with an ice-methanol bath. This may or may not have been a significant improvement. The new method of work-up of the crude products, developed during this study, is a definite improvement and has resulted in higher yields of purified product and significantly less decomposition. This new method consists of recrystallization of the products from methylene chloride-ethanol at or below room temperature.

2. Synthesis of meta-(2-vinyloxy)ethoxy-β-nitrostyrene.-- This compound was successfully synthesized, isolated, and characterized. The compound was successfully obtained by varying only the method of recrystallization of the crude product. Due to the apparently high reactivity of the vinyloxy group on this compound, it cannot be recrys tallized from a warm protic solvent. The desired compound was recrys tallized from carbon tetrachloride below room temperature to give a 90 percent yield.

B. Cationic Polymerizations of Ortho, Meta, and Para-(2-vinyloxy)ethoxy-β-nitrostyrene

All monomers were found to polymerize in the presence of $BF_3$ in a dry solvent under nitrogen at $-78^\circ C$. The polymers obtained were yellow amorphous solids and were linear polymers as indicated by their solubility in methylene chloride. The polymers were found to be only sparingly soluble in acetone and insoluble in all solvents tested that were less polar than acetone.

The infra-red spectra of the polymers lacked the 1620 and 1640 $cm^{-1}$ absorptions typical of the monomers while the absorptions assigned to the nitrovinyl moeity (1625-1640 $cm^{-1}$) were still present.

The apparent success of these selective cationic polymerizations of the electron-rich pendant vinyloxy groups would seem to indicate that such selective cationic polymerizations should be general in application. The obvious requirement of such a system is that the electron-poor moeity be unreactive toward carbonium ions.

The polymers of the meta and para isomers cross-linked in methylene chloride upon reaction with sodium ethoxide to give quantitative yields of insoluble amorphous resins. The infra-red spectrum of the cross-linked polymer of the para isomer gave no detectable nitrovinyl absorption while the corresponding meta isomer seemed to have some pendant nitrovinyl groups still intact.

C. Anionic Polymerizations of Ortho, Meta, and Para-(2-vinyloxy)ethoxy-β-nitrostyrene

The ortho isomer gave no ethanol insoluble product and recovery of monomer was almost quantitative. This observation was expected in view of the "ortho-effect" reported by Nash[13] and Drueke.[7]

The meta and para isomers both gave high conversions to ethanol insoluble product. The resulting polymers were white powders whose infra-red spectra indicated that the vinyloxy groups were yet intact as indicated by the 1620 and 1640 $cm^{-1}$ absorptions.

The polymers were found to form amber solutions in hexamethyl-phosphotriamide (HMPA) and N,N-dimethylaniline, thus facilitating the determination of intrinsic viscosities and purification by reprecipita-tion. Unfortunately, these solvents deactivate cationic initiators and thus are unsuitable solvents for cross-linking polymerizations with Lewis acids. This solubility is probably the result of an interaction between the non-bonded electrons on nitrogen (solvent) and the electron deficient nitro group (polymer). The exact nature of this interaction is not presently understood.

D. The Possible Existence of an Intramolecular Interaction and Six-membered Ring Formation by Para-(2-vinyloxy)ethoxy-β-nitrostyrene

The infra-red spectrum of this compound was examined in detail, both in the solution phase ($CH_2Cl_2$) and the solid phase (Nujol mull and KBr pellet). In all cases, its spectrum included a strong absorption at 1629 $cm^{-1}$ and a barely perceptible shoulder at 1640 $cm^{-1}$ for the vinyloxy group. The 1640 $cm^{-1}$ absorption was almost undetectable due to the strong broad 1630 $cm^{-1}$ absorption due to the nitrovinyl moeity. The validity of the 1630 $cm^{-1}$ assignment was demonstrated by comparison with the spectrum of para-methoxy- -nitrostyrene.

In order to demonstrate the validity of the 1640 $cm^{-1}$ shoulder assignment, para-nitro-(2-vinyloxy)ethoxybenzene was synthesized. This compound is electronically similar to the compound in question and if the ring-form exists in the β-nitrostyrene, it should also exist in this

compound. The infra-red spectrum of this compound contains a medium absorption at 1640 cm.$^{-1}$ The spectrum of each compound is shown in Figure 4, page 61, and pertinent infra-red data of these and other compounds appears in Table 5, page 62.

Assuming that the postulate of Brey and Tarrant,[14] which states that these two absorptions are due to the two rotational isomers of the vinyloxy group, is valid, then the infra-red data obtained in this study indicates that the ring-form is not the sole existing form of the molecule.

During the course of this study, the $^{1}$H nmr spectra of the three vinyloxyethoxy-β-nitrostyrenes, para-nitro-vinyloxyethoxybenzene, (2-vinyloxy)ethoxybenzene, and β-chloro-ethyl vinyl ether were examined in detail. The spectra of the vinyloxy groups, in particular, were of interest. The geminal coupling constants ($J_{AB}$), the cis coupling constants ($J_{AC}$), and the trans coupling constants ($J_{BC}$), and the chemical shifts of the -protons ($H_c$) were obtained. See Table 6a, page 63.

$$\underset{RO}{\overset{H_C}{\diagdown}}C=C\underset{H_B}{\overset{H_A}{\diagup}}$$
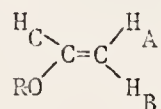
The geminal coupling constant of para-(2-vinyloxy)ethoxy-β-nitrostyrene ($J_{AB}$ = -2.2 hz.) is less than that of (2-vinyloxy)ethoxybenzene ($J_{AB}$ = -2.0 hz.) and equal to that of meta-(2-vinyloxy)ethoxy-β-nitrostyrene ($J_{AB}$ = -2.2 hz.). This indicates that the degree of resonance (or extent of mesomeric contribution) existing in the para isomer is approximately equal to that of the meta isomer and significantly less than that in (2-vinyloxy)ethoxybenzene.

The cis coupling constant for the para isomer ($J_{AC}$ = 7.0 hz.) was higher than both the meta isomer (6.9 hz.) and the ortho isomer
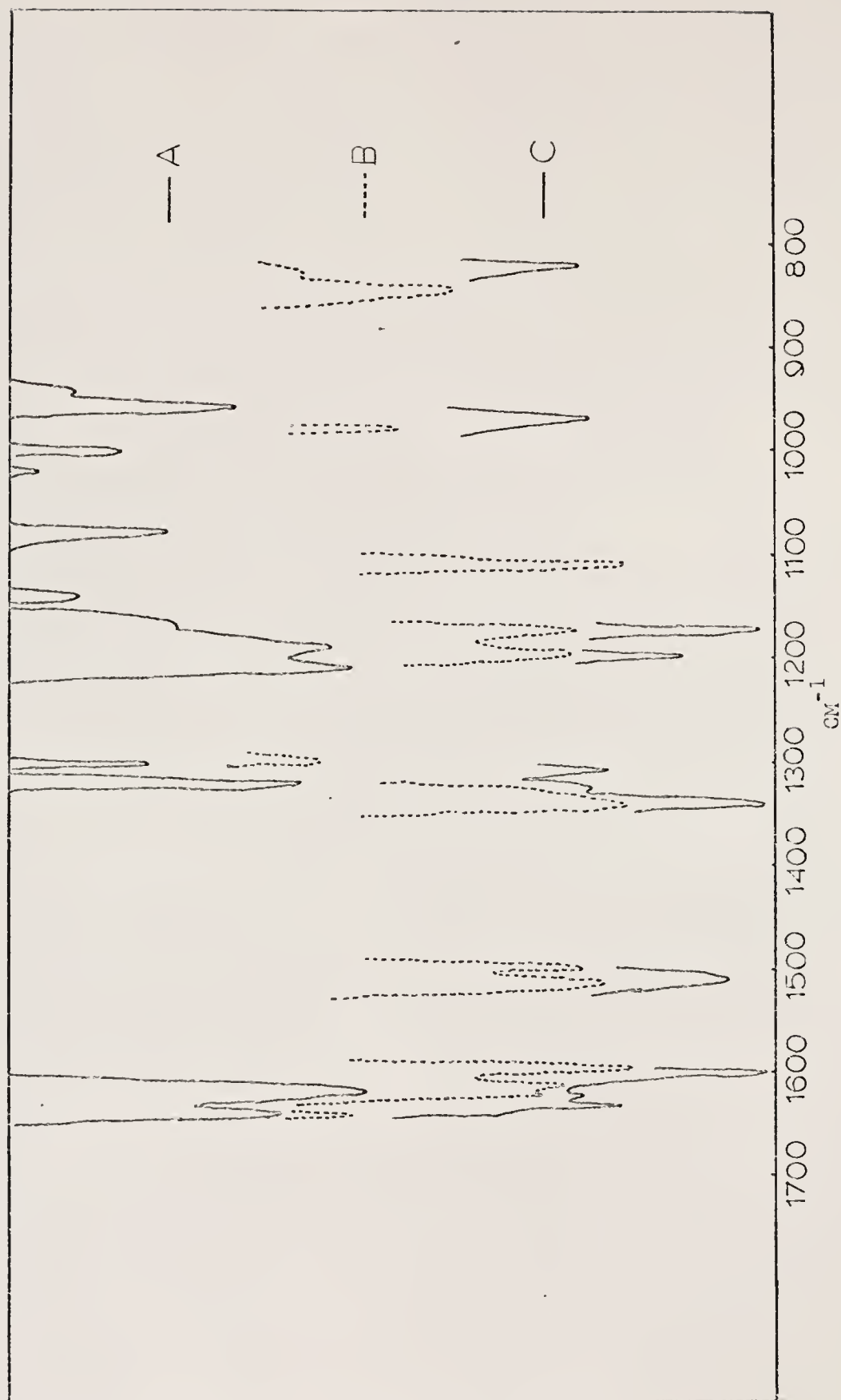
Figure 4

Major Infra-red Absorptions of β-chloroethyl Vinyl Ether (A), Para-nitro-(2-vinyloxy)-ethoxybenzene (B), and Para-(2-vinyloxy)ethoxy-β-nitrostyrene (C)

## TABLE 5

Pertinent Infra-red Data of Monomers, Polymers and Related Compounds

| Compound | C=C nitrovinyl (cm$^{-1}$) | C=C vinyloxy (cm$^{-1}$) | C=C aromatic (cm$^{-1}$) |
|---|---|---|---|
| 1. ortho-(2-vinyloxy)ethoxy -β-nitrostyrene | 1625 | 1620, 1640 | 1595 |
| 2. meta-(2-vinyloxy)ethoxy -β-nitrostyrene | 1640[*] | 1620, 1640[*] | 1601, 1610 |
| 3. para-(2-vinyloxy)ethoxy -β-nitrostyrene | 1630 | 1620, 1640[**] | 1603 |
| 4. ortho-methoxy- β-nitrostyrene | 1625 | | 1595 |
| 5. meta-methoxy- β-nitrostyrene | 1640 | | 1595, 1605 |
| 6. para-methoxy- β-nitrostyrene | 1623 | | 1600 |
| 7. para-nitro-(2-vinyloxy) ethoxybenzene | | 1620, 1640 | 1595, 1610 |
| 8. number 1 cationically polymerized | 1625 | | 1595 |
| 9. number 2 cationically polymerized | 1640 | | 1602 |
| 10. number 3 cationically polymerized | 1630 | | 1603 |
| 11. number 2 anionically polymerized | | 1620, 1640 | 1560, 1600 |
| 12. number 3 anionically polymerized | | 1620, 1640 | 1560, 1600 |
| 13. number 9 cross-linked | | | 1608 |
| 14. number 10 cross-linked | | 1640 (weak) | 1600 |

[*] overlapping absorption
[**] shoulder

## TABLE 6a

### Nuclear Magnetic Resonance Data from Some Vinyloxy Compounds
### $(CDCl_3, 60 Mc./sec.)$

$$\begin{array}{c} H \\ R-O \end{array} C=C \begin{array}{c} H \\ H \end{array}$$

| Compound | $\tau Hc$ | $J_{AC}$(hz.) (cis) | $J_{BC}$(hz.) (trans) | $J_{AB}$(hz.) (gem) |
|---|---|---|---|---|
| ortho-(2-vinyloxy)ethoxy-β-nitrostyrene | 3.42 | 6.9 | 14.0 | -2.4 |
| meta-(2-vinyloxy)ethoxy-β-nitrostyrene | 3.46 | 6.9 | 14.2 | -2.2 |
| para-(2-vinyloxy)ethoxy-βnitrostyrene | 3.43 | 7.0 | 14.3 | -2.2 |
| para-nitro-(2-vinyloxy)-ethoxybenzene | 3.42 | 6.9 | 14.2 | -2.4 |
| (2-vinyloxy)ethoxybenzene | 3.53 | 6.9 | 14.0 | -2.0 |
| β-chloroethyl vinyl ether | 3.55 | 7.0 | 14.2 | -2.3 |

## TABLE 6b

### Nuclear Magnetic Resonance Data from Some Vinyl Ethers*

| R | $\tau Hc$ | $J_{AC}$(hz.) | $J_{BC}$(hz.) | $J_{AB}$(hz.) |
|---|---|---|---|---|
| t-butyl | 3.72 | 6.2 | 13.2 | -0.1 |
| i-propyl | 3.75 | 6.9 | 13.7 | -1.2 |
| cyclohexyl | 3.87 | 5.7 | 14.7 | -1.6 |
| 2-ethylhexyl | 3.60 | 6.1 | 12.9 | -1.8 |
| i-butyl | 3.56 | 6.3 | 14.2 | -1.7 |
| n-butyl | 3.47 | 6.9 | 14.4 | -1.8 |
| ethyl | 3.55 | 6.9 | 14.9 | -1.7 |
| methyl | 3.62 | 6.6 | 14.4 | -2.2 |
| β-chloroethyl | 3.50 | 6.6 | 16.2 | -2.7 |

*Data of Feeney and coworkers[33]
(Neat, 40 Mc./sec.)

(6.9 hz.) and equal to that of the corresponding para-substituted-nitro benzene (7.0 hz.). A similar trend was noted in the trans coupling constants. The trans coupling constant for para-(2-vinyloxy)ethoxy-$\beta$-nitrostyrene ($J_{BC}$ = 14.3 hz.) was the highest obtained for any of the six compounds studied.

The chemical shift of the $\alpha$-proton of the para isomer ($\tau$ = 3.43) was quite similar to that of the corresponding nitrobenzene ($\tau$ = 3.42) as well as that of the ortho isomer ($\tau$ = 3.42). At the same time it was significantly downfield from the corresponding signal of the meta isomer ($\tau$ = 3.46), vinyloxyethoxybenzene ($\tau$ = 3.53), and $\beta$-chloroethyl vinyl ether ($\tau$ = 3.55).

These trends indicate that any possible contribution of the ring conformation does not significantly affect the over-all degree of resonance present. It also appears that the degree of oxonium character present in the phenolic oxygen in both the ortho and para isomers does influence the degree of resonance via an inductive effect through the two carbon saturated bridge. This would also explain why the vinyloxy groups of the ortho and para isomers are so much less reactive toward electrophilic attack (as evidenced by their stability in warm ethanol) than the meta isomer.

The ultra-violet spectrum of the cationically initiated polymer of the para isomer was found to be quite similar to that of the parent compound (see Figure 5, page 65). The absorption maxima were at identical wavelengths and only the molar absorption coefficients varied. This agreed well with the results of Thompson who compared the spectrum of the para isomer with the corresponding para-(2-ethyloxy)ethoxy-$\beta$-nitro-styrene. These results again give no indication of any intramolecular interaction in the vinyloxy compound.
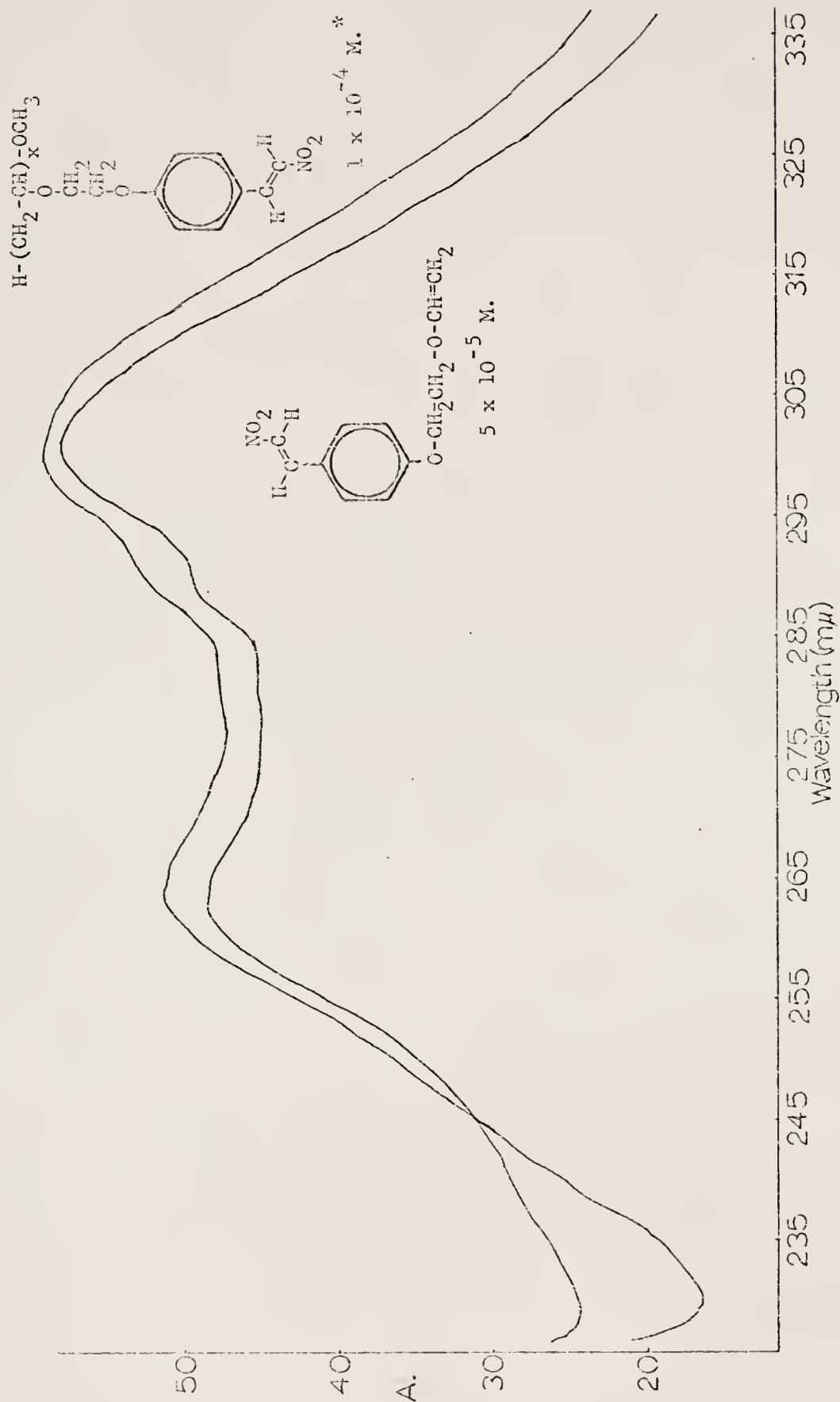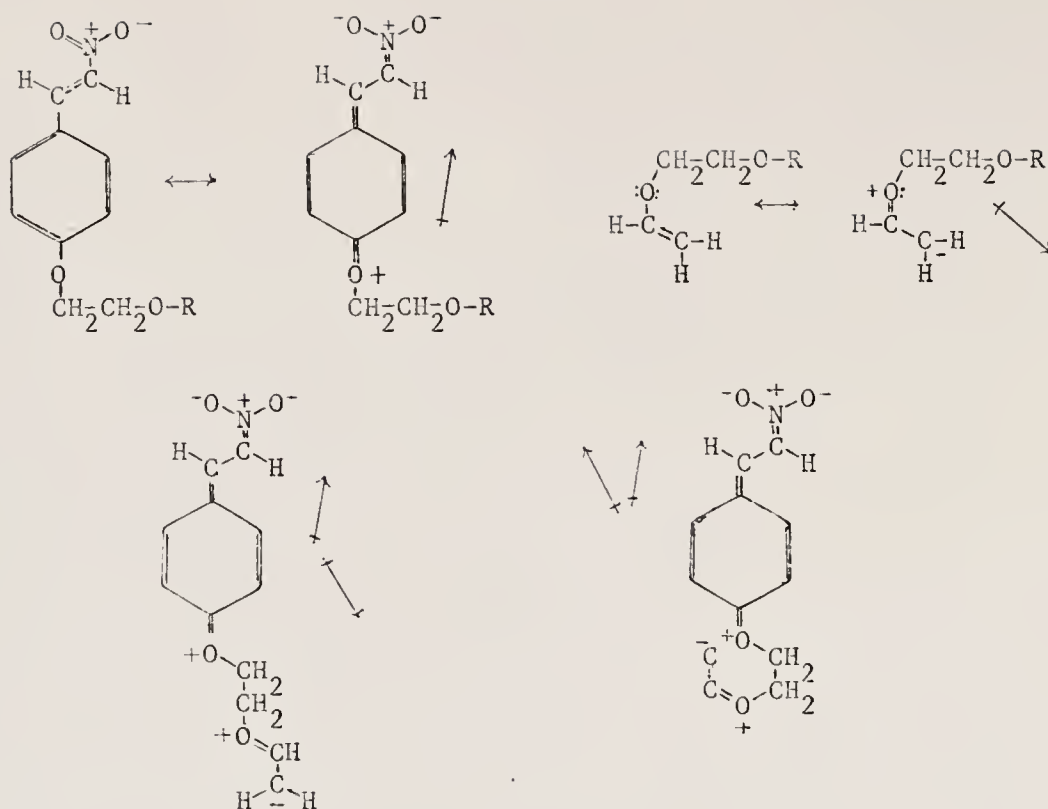
Figure 5

The Ultra-violet spectra of Para-(2-vinyloxy)ethoxy-β-nitrostyrene and the Cationically initiated Polymer of That Compound (Methylene Chloride)

The results of these studies prompted the author to examine more closely some of the results and conclusions reported by Thompson. Thompson has pointed out that the inductive effect across a saturated two-carbon bridge is much less than across a one-carbon bridge. It should be pointed out that the difference in pKa between acetic acid and β-chloropropionic acid (0.80) means that the Ka of the latter acid is 6.3 times greater. In addition, the Ka of the latter acid is 7.6 times larger than that of propionic acid.

Perhaps a more pertinent comparison, for the purpose of gaining some insight into the sensitivity of the vinyloxy group to inductive effects, can be made by examining the rates of acid catalyzed hydration of certain vinyl ethers as both reactions involve a rate-determining attack by an electrophile to produce analogous carbonium ions. Jones and Wood[8] have reported that the rate of hydrolysis of ethyl vinyl ether is $5.3 \times 10^{-2}$ 1. mole$^{-1}$ sec.$^{-1}$ while that of β-chloroethyl vinyl ether is $0.44 \times 10^{-2}$ 1. mole$^{-1}$ sec.$^{-1}$. This data indicates that vinyl ethers are quite sensitive to inductive effects, even when such effects must be transmitted across a saturated two-carbon bridge.

This author considers the dipole moment data determined by Thompson as evidence against the proposed ring-form. The reasoning behind this statement may best be explained by considering para-(2-vinyl-oxy)ethoxy-β-nitrostyrene as a di-substituted ethylene glycol. One may thus consider the dipole moment of the compound to be the resultant of the two vectors which in turn represent the "group moments" of the two "substituents".

$$O\diagdown \overset{+}{N}\diagup O^{-}$$

H–C≎C–H

⟷

$$^{-}O\diagdown \overset{+}{N}\diagup O^{-}$$

H–C=C–H

↑

O

CH$_2$CH$_2$O–R

O+

CH$_2$CH$_2$O–R

CH$_2$CH$_2$O–R

:O:

H–C=C–H
  |
  H

⟷

CH$_2$CH$_2$O–R

$\overset{+}{O}$:

H–C–C–H
  |
  H

↘

$$^{-}O\diagdown \overset{+}{N}\diagup O^{-}$$

H–C=C–H

↑

+O
  CH$_2$
  CH$_2$
+O=CH
   C–H
  H  H

$$^{-}O\diagdown \overset{+}{N}\diagup O^{-}$$

H–C=C–H

↖ ↑

–C  +O  CH$_2$
–C=O  CH$_2$
  +

If the vinyloxy group is not involved in a ring-form, then
its time-average resultant position in space would require that the
angle between the two group moments be greater than 90°, assuming extremely
hindered rotation between the phenyl oxygen, and about 180° assuming
free rotation about that bond.

On the other hand, one would expect the angle between the two
group moments to be quite small if one assumes the ring-form. Thus,
from a qualitative stand point, the resultant dipole moment of the ring-
form would be expected to be greater than that of the corresponding
ethyloxy compound while one would expect the linear-form to have a
dipole moment less than the ethyloxy compound. The dipole moment of the
ethyloxy compound is greater by 0.71 D.

In conclusion, the data obtained to date indicates that the
postulated ring-form, if existent, is not the sole existing form of the

molecule. The data, however, does not rule out an equilibrium between the linear-form and ring-form. However, it would appear that the inductive effect of the partial oxonium, through the saturated two carbon bridge, exerts the predominant effect on the physical and spectral properties of the molecule.

## Studies of the Anionic Polymerization of Some Other Mono-substituted β-nitrostyrenes

### A. Synthesis of Compounds

Fifteen substituted β-nitrostyrenes and β-nitrostyrene were synthesized for this study, all of which had been previously described in the literature. All compounds were synthesized by the methods of Thompson, however, rather than the various methods described for the known compounds. For this reason the results of all syntheses were described. In general the yields of purified monomer were poor, not because of the method of synthesis but because of the method of recrystallization which nearly always involved hot or warm ethanol. In most cases, the process of dissolving the crude product in hot ethanol was accompanied by an undesirable side reaction which reduced some product to an amorphous white solid (probably polymer).

It is unfortunate that the technique of recrystallization from methylene chloride and ethanol at room temperature (as described in the synthesis of ortho-(2-vinyloxy)ethoxy-β-nitrostyrene) had not yet been discovered. It is very likely that this technique would have resulted in much higher yields of purified monomer, particularly in the case of the more polar compounds.

## B. Kinetic Study of the Polymerization Rates

The method (gravimetric) used to determine the rates is less than ideal. The major disadvantage is that rates of polymerization are determined from precipitated product and the accuracy of the determination obviously relies heavily upon an essentially quantitative precipitation of the product. Furthermore, when the percent conversions are very low, a very small amount of polymer left in solution can be very significant. Most of the polymers obtained during this study were essentially insoluble in all common organic solvents tested except DMF. Of course, polymer solubility is dependent on molecular weight. The solubility of lower molecular weight polymers is always greater. The molecular weight distribution curves of polymer samples obtained during this study indicate that molecular weights are extremely uniform as indicated by the low values for $\overline{M}_w/\overline{M}_n$ obtained (see Table 7 on page 70. A notable exception to this was poly-meta,$\beta$-dinitrostyrene. Low ratios of $\overline{M}_w/\overline{M}_n$ and narrow molecular weight distributions are typical for anionic polymerizations in aprotic media where chain transfer and termination are not occurring.

The elemental analyses of the polymers obtained during this study appear in Table 8, page 71, and the melt temperatures in Table 9, page 72. The polymers evidenced unexpected thermal stability. The other assumptions incorporated in the kinetic treatment well be discussed individually.

1. The rate of initiation is fast relative to propagation.--
Two fairly representative monomers, para-methoxy-$\beta$-nitrostyrene and $\beta$-nitrostyrene, were quantitatively investigated in this respect. Para-methoxy-$\beta$-nitrostyrene in particular was studied because it apparently

TABLE 7

Results of Molecular Weight Distribution Analysis* of Some
Poly-β-nitrostyrenes by Gel Permeation Chromatography (GPC)

| Polymer | Source** of | Number Average Molec. Length $\bar{A}_n$ (Å) | Weight Average Molec. Length $\bar{A}_w$ (Å) | $\bar{A}_w/\bar{A}_n$ | Number Average Molec. Weight $\bar{M}_n$ | Weight Average Molec. Weight $\bar{M}_w$ | $\bar{M}_w/\bar{M}_n$ |
|---|---|---|---|---|---|---|---|
| Para-methyl | Run 4 | 115 | 151 | 1.31 | 5,000 | 6,600 | 1.32 |
| Meta-methoxy | Run 4 | 133 | 159 | 1.15 | 6,000 | 7,000 | 1.17 |
| Para-fluoro | Run 4 | 166 | 355 | 2.14 | 7,000 | 10,500 | 1.50 |
| Ortho-fluoro | Run 3 | 103 | 139 | 1.35 | 4,500 | 6,000 | 1.33 |
| Para-chloro | Run 3 | 61 | 77 | 1.27 | 2,750 | 3,500 | 1.27 |
| Meta-bromo | Run 4 | 95 | 161 | 1.69 | 4,200 | 7,800 | 1.62 |
| Para-bromo | Run 4 | 45 | 101 | 2.26 | 1,800 | 3,500 | 1.95 |
| Meta-nitro | Run 1 | 211 | 1,730 | 8.20 | 9,500 | 70,100 | 7.38 |

*   Calculations are based on calibration curves derived from standard polystyrene samples.

**  Polymers analyzed are products from the kinetic study.  See Table 1, page 37.

TABLE 8

Elemental Analyses of Poly-β-nitrostyrenes

| Substituent | Theoretical | | | | Experimental | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | %C | %H | %N | %Halogen | %C | %H | %N | %Halogen | %Residue |
| H | 64.42 | 4.73 | 9.39 | - | 64.45 | 4.85 | 9.22 | - | - |
| meta-methyl | 66.24 | 5.55 | 8.58 | - | 65.10 | 5.39 | 8.42 | - | - |
| para-methyl | 66.24 | 5.55 | 8.58 | - | 65.17 | 5.48 | 8.26 | - | - |
| meta-methoxy | 60.33 | 5.06 | 7.81 | - | 60.27 | 5.24 | 7.71 | - | - |
| para-methoxy | 60.33 | 5.06 | 7.81 | - | 60.43 | 5.16 | 7.67 | - | - |
| ortho-fluoro | 57.48 | 3.61 | 8.38 | 11.36 | 56.95 | 3.48 | 7.24 | 10.48 | - |
| meta-fluoro | 57.48 | 3.61 | 8.38 | 11.36 | 54.73 | 3.60 | 7.69 | - | 2.82 |
| para-fluoro | 57.48 | 3.61 | 8.38 | 11.36 | 57.69 | 3.76 | 8.26 | - | - |
| para-chloro | 52.33 | 3.29 | 7.63 | 19.31 | 52.15 | 3.43 | 7.59 | 19.03 | - |
| meta-bromo | 42.13 | 2.65 | 6.14 | 35.04 | 42.21 | 2.79 | 5.93 | 34.83 | - |
| para-bromo | 42.13 | 2.65 | 6.14 | 35.04 | 42.33 | 2.88 | 5.92 | 34.84 | - |
| meta-nitro | 49.99 | 3.11 | 14.43 | - | 49.23 | 3.58 | 13.46 | - | - |
| para-nitro | 49.49 | 3.11 | 14.43 | - | 49.73 | 3.73 | 13.01 | - | - |

TABLE 9

Thermal Behavior of Poly-substituted-β-nitrostyrenes

| Substituent | Discoloration of Solid °C. | Melt Temperature °C. |
|---|---|---|
| H | - | 300-305 (dec.) |
| meta-methyl | 275-280 | >300 |
| para-methyl | 295 | >300 |
| meta-methoxy | - | 290-295 (dec.) |
| para-methoxy | 260 | 270-275 (dec.) |
| ortho-fluoro | 285-295 | >300 |
| meta-fluoro | 275-280 | >300 |
| para-fluoro | 290-295 | >300 |
| para-chloro | 285-290 | >300 |
| meta-bromo | 250-260 | >300 |
| para-bromo | 280-290 | >300 |
| meta-nitro | - | 290-295 (dec.) |
| para-nitro | - | 290-300 (dec.) |

is the least reactive of all monomers studied. It was felt that if
this monomer would "pass the test" then the assumption is probably
valid. The ultra-violet method used gave values for the rate constant
of initiation, $k_i$ = 2.9 and 3.5 1. mole$^{-1}$ sec.$^{-1}$, respectively, for the
para-methoxy and non-substituted $\beta$-nitrostyrenes (see Figures 6 and 7,
pages 74 and 75. These values indicate that the rate of initiation is
rapid and that the observed rate of polymerization, $\nu_p$, is the rate of
propagation.

    2.   The rate of chain transfer is small or non-existent.--
As previously mentioned, those polymers whose solubility in DMF per-
mitted GPC molecular weight distribution analysis gave very narrow
molecular weight distributions (see Figure 8, page 76, for a typical
example). This is one of the most surprising characteristics of these
polymerizations to be noted to date. The apparent lack of reactivity
of the propagating $\beta$-nitrostyryl carbanion toward ethanol can be ration-
alized on the basis of pKa values. The pKa of nitromethane is 11.0
while that of ethanol is 15.9. It can be seen that the structure of
the propagating $\beta$-nitrostyryl carbanion is quite analogous to that of
the conjugate base of nitromethane. From this data it can be seen that
the propagating carbanion is a far weaker base than the ethoxide anion.

    3.   Termination does not occur during the polymerizations.--
The molecular weight distribution data also supports this assumption
except in the case of the meta and para-$\beta$-dinitrostyrenes where a "back
biting" form of auto-termination has been proposed. This termination
also accounted for the broader molecular weight distribution curves for
the corresponding polymers (see Figure 24, page 102). In higher concen-
trations of polymer, intermolecular termination is also likely.
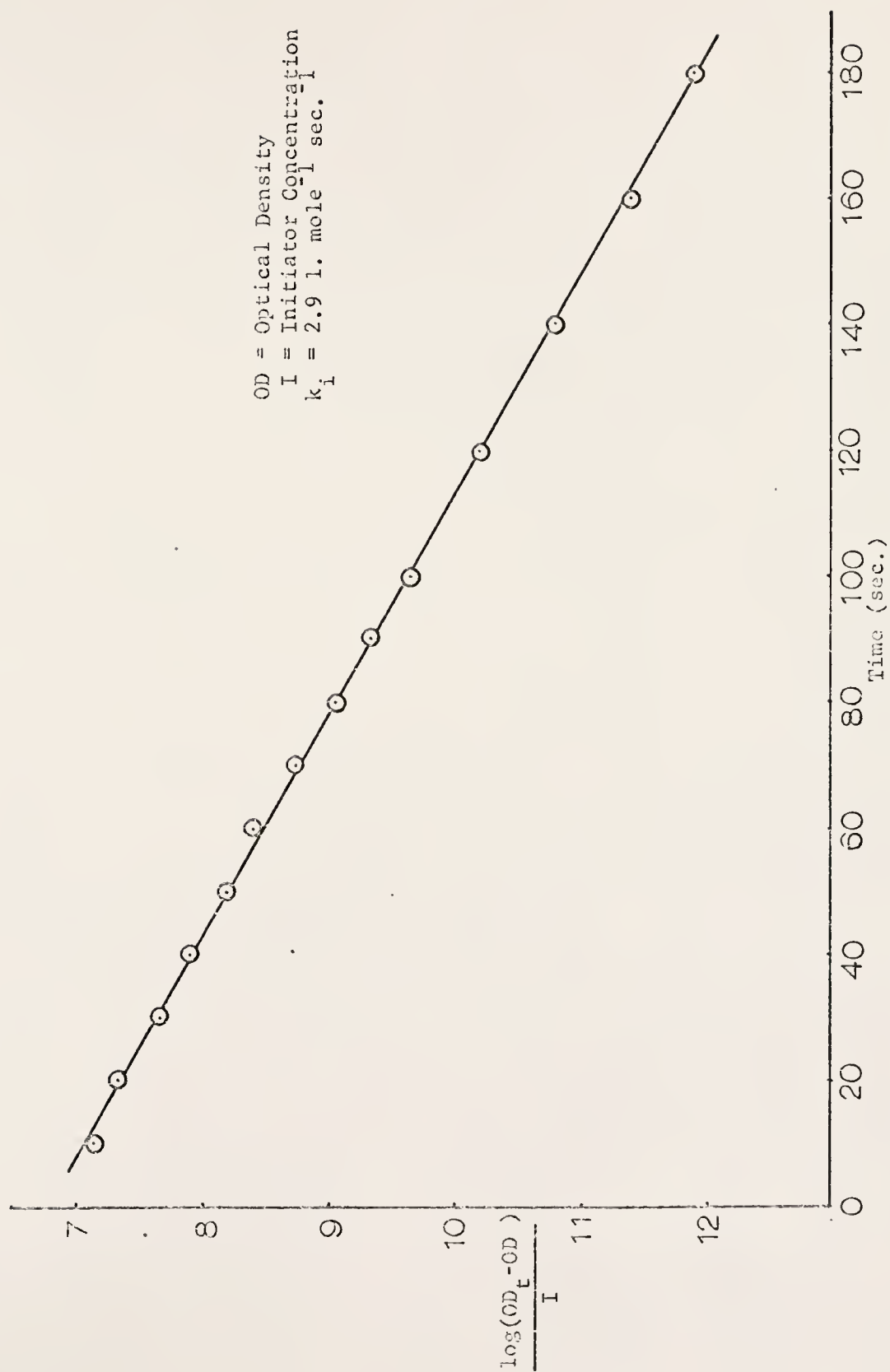
Kinetics of the Rate of Initiation of Para-methoxy-β-nitrostyrene by Sodium Ethoxide

Figure 6

$k_i = 3.5$ l. mole$^{-1}$ sec.$^{-1}$
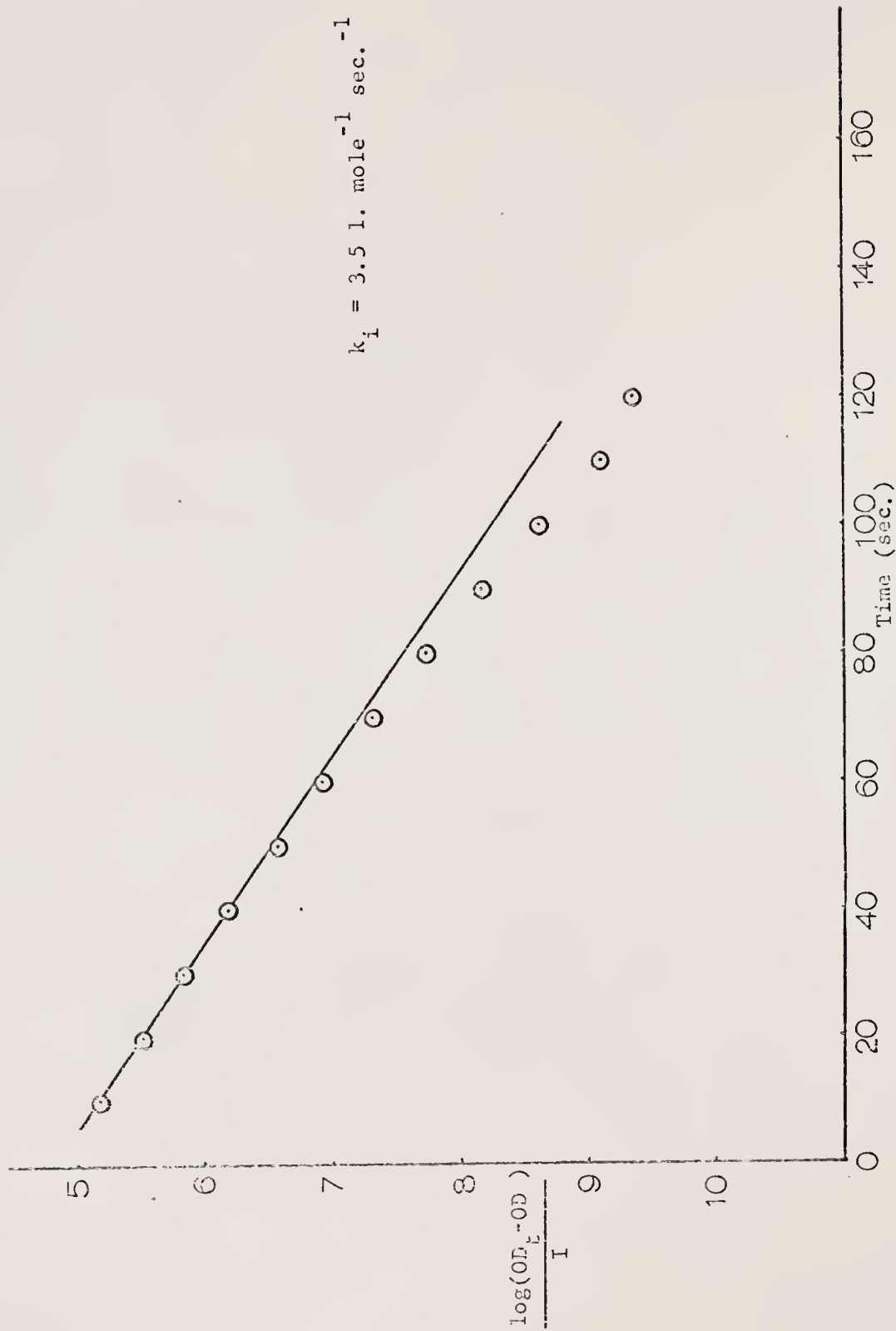
Kinetics of the Rate of Initiation of $\beta$-nitrostyrene by Sodium Ethoxide

Figure 7

$\frac{\log(OD_t - OD)}{I}$

Time (sec.)
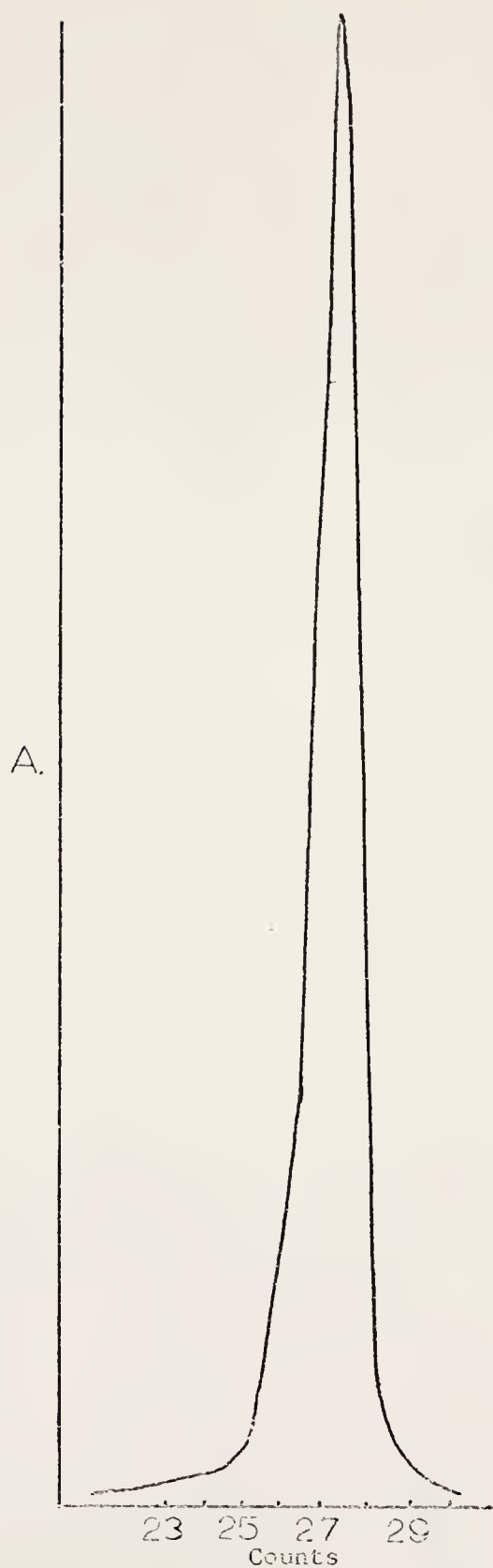
Figure 8

Molecular Weight Distribution Curve of Poly-para-
chloro-ß-nitrostyrene

The fact that termination does occur for these monomers coupled with the apparently significant solubility of the resulting polymers in the chosen solvent system made it impossible to obtain a rate constant for para-$\beta$-dinitrostyrene. The validity of the value obtained for the meta isomer should be questioned despite its excellent Hammett plot agreement with that value obtained by Kamlet and Glover.[19]

4, 5. <u>The length of the polymer chain does not affect the rate of reaction.</u>-- This assumption appears to be valid up to a point as indicated by the kinetic plots (see Figures 6-15, pages 74 through 84.) The "straight-line behavior" of the data indicates that this assumption is valid for low conversions. As previously mentioned, the polymerizations are heterogeneous after 10 to 25 seconds of polymerization depending upon the monomer. This requires that, in order to maintain a constant rate of polymerization, the propagating carbanion must maintain a constant access to monomer which becomes more difficult as the length of the precipitating polymer occludes and effectively buries the carbanion. This is the most probable explanation for the sudden decrease in observed rates of polymerization at higher percent conversion. However, the fact that the observed rates remain constant past the point of heterogeneity does definitely show that the more precipitation of product does not alter the kinetics of the reaction. This observation validates assumption 5 as well.

6. <u>Conversion of initiator to propagating carbanion is quantitative and the reactivity of all resulting ion-pairs is assumed to be equal.</u>-- The initiation reaction must be quantitative as evidenced by the relatively high reactivity of $\beta$-nitrostyrenes toward nucleophilic attack. This high reactivity is apparent from Kamlet's[18] observations.

slope = $\nu_p$ = 11.8 x $10^{-5}$ moles l.$^{-1}$ sec.$^{-1}$

$\nu_p$ = $k_p$ [M][M$^-$]

[M$^-$] = [I] = [ethoxide] = 5.25 x $10^{-4}$ M.

[M] = monomer conc. = 0.250 M.

$k_p$ = 0.90 l. mole$^{-1}$ sec.$^{-1}$

[P]* x $10^3$

10.00

7.50

5.00

2.50

0

0    0.5    1.0    1.5    2.0

Time (min.)
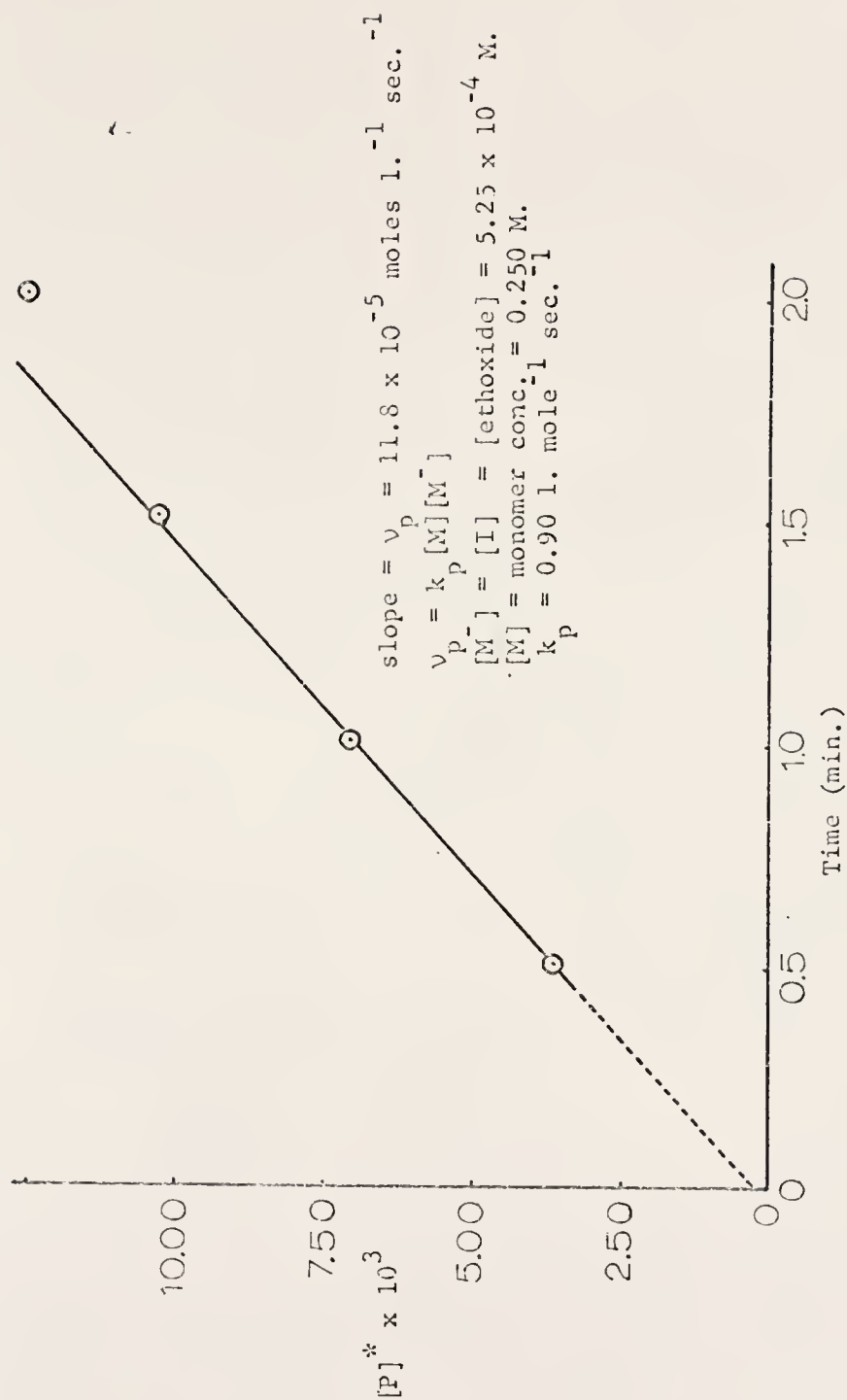
Figure 9

Kinetics of the Anionic Polymerizations of β-nitrostyrene

*[P] is expressed in terms of moles of monomer units/liter converted to polymer. Note that each increment of the ordinate represents 1 percent conversion.
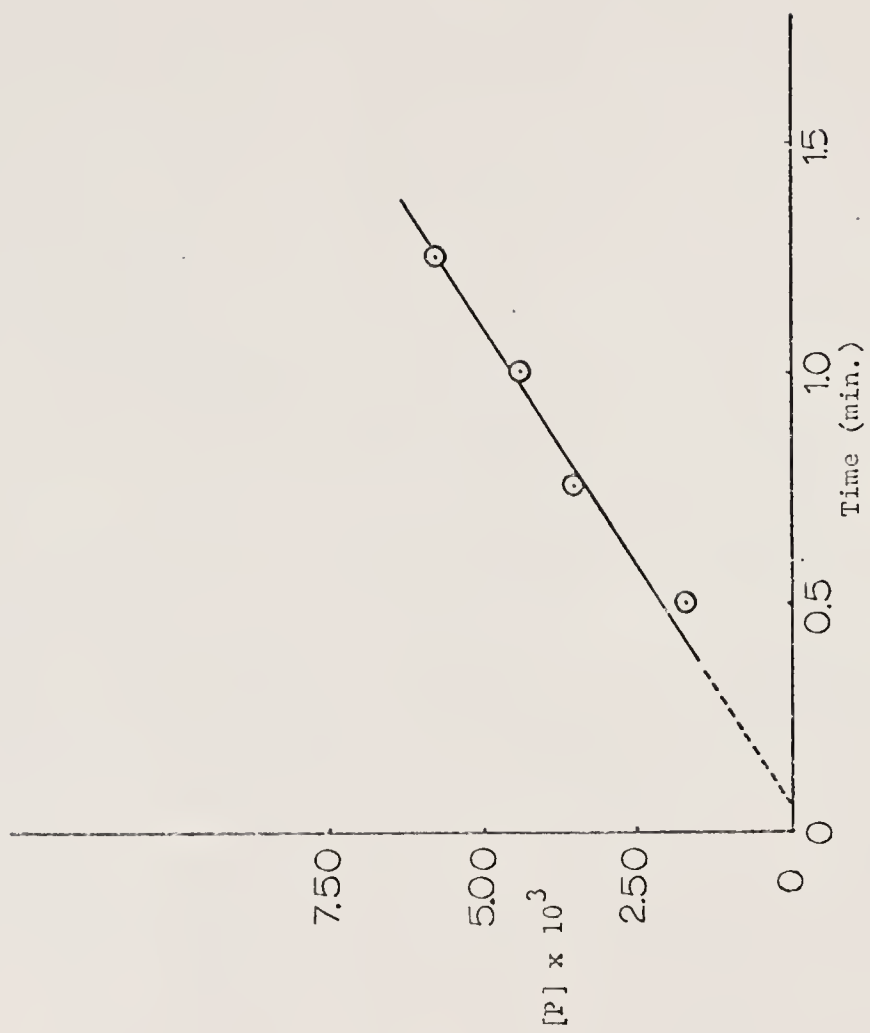
Figure 10

Kinetics of the Anionic Polymerization of Meta-methyl-β-nitrostyrene

Figure 11

Kinetics of the Anionic Polymerization of Para-methyl-β-nitrostyrene
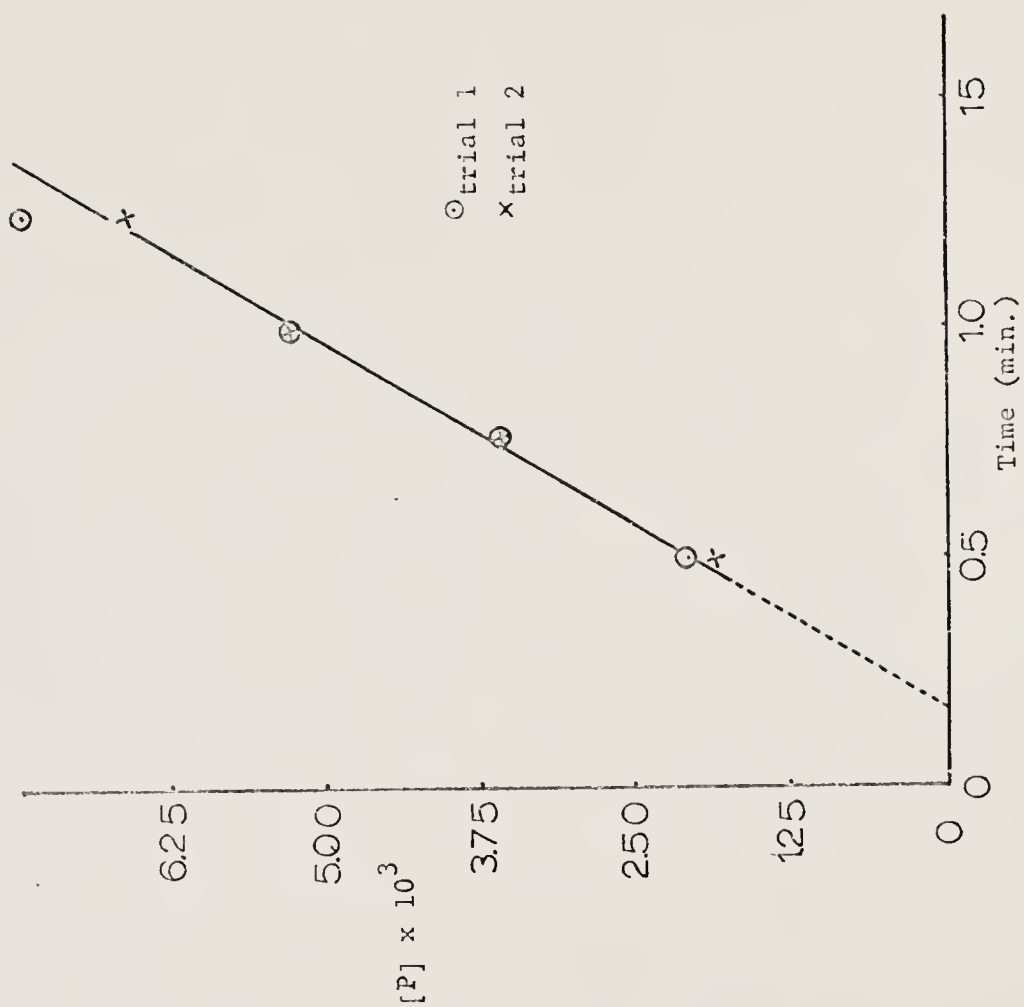
Figure 12

Kinetics of the Anionic Polymerization of Meta-methoxy-β-nitrostyrene
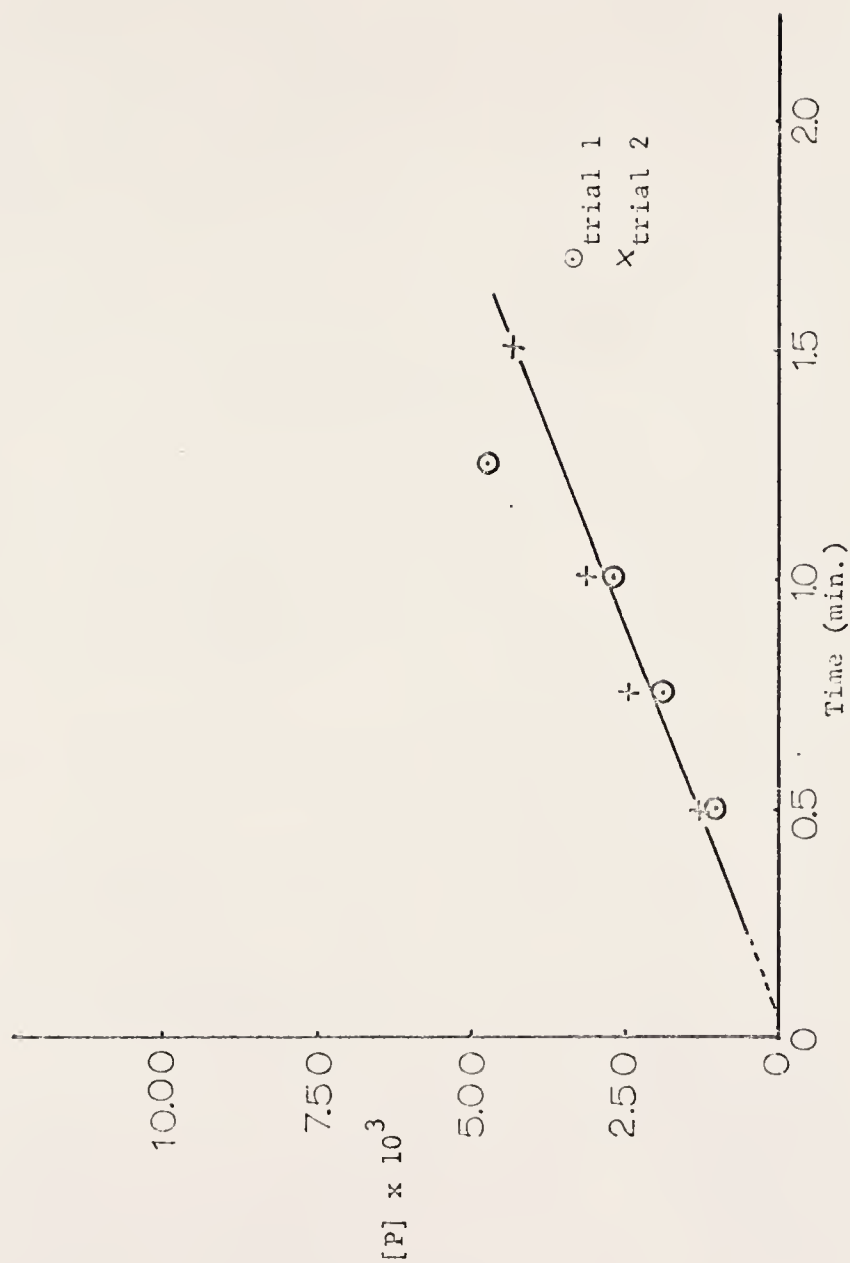
Figure 13

Kinetics of the Anionic Polymerization of Para-methoxy-$\beta$-nitrostyrene
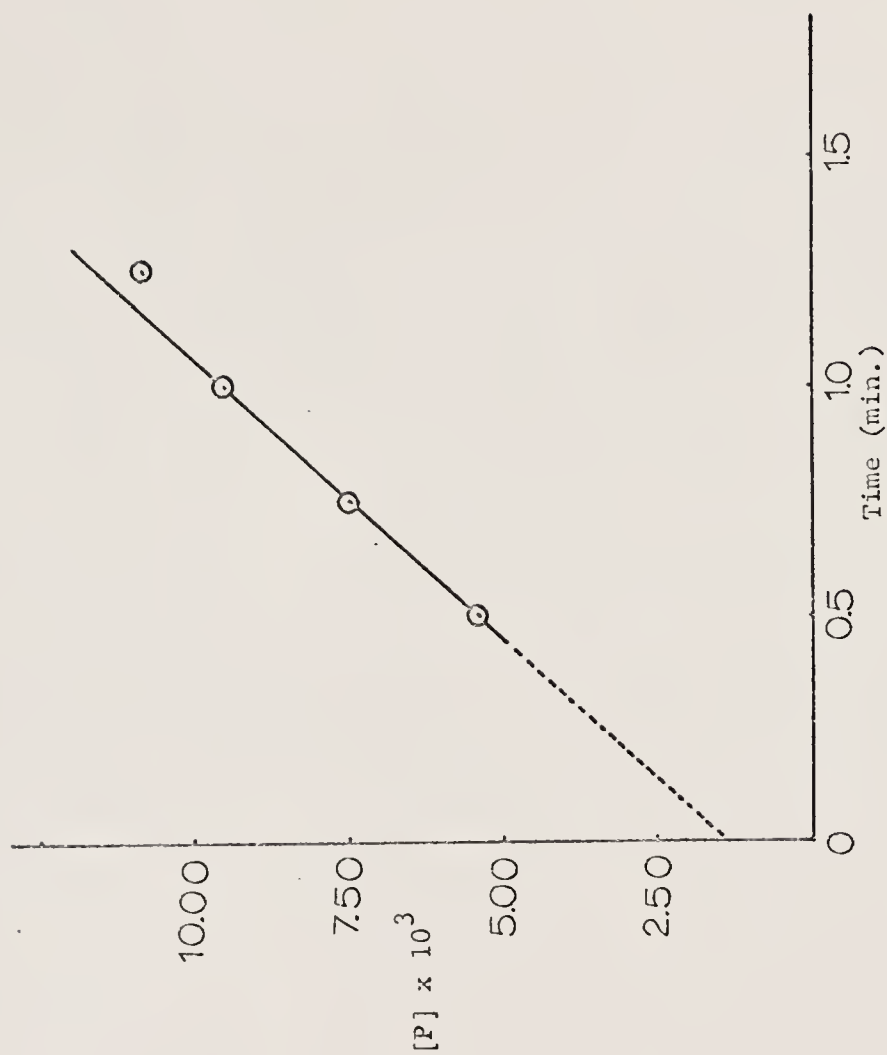
Figure 14

Kinetics of the Anionic Polymerization of Para-fluoro-β-nitrostyrene

Figure 15

Kinetics of the Anionic Polymerization of Para-chloro-β-nitrostyrene
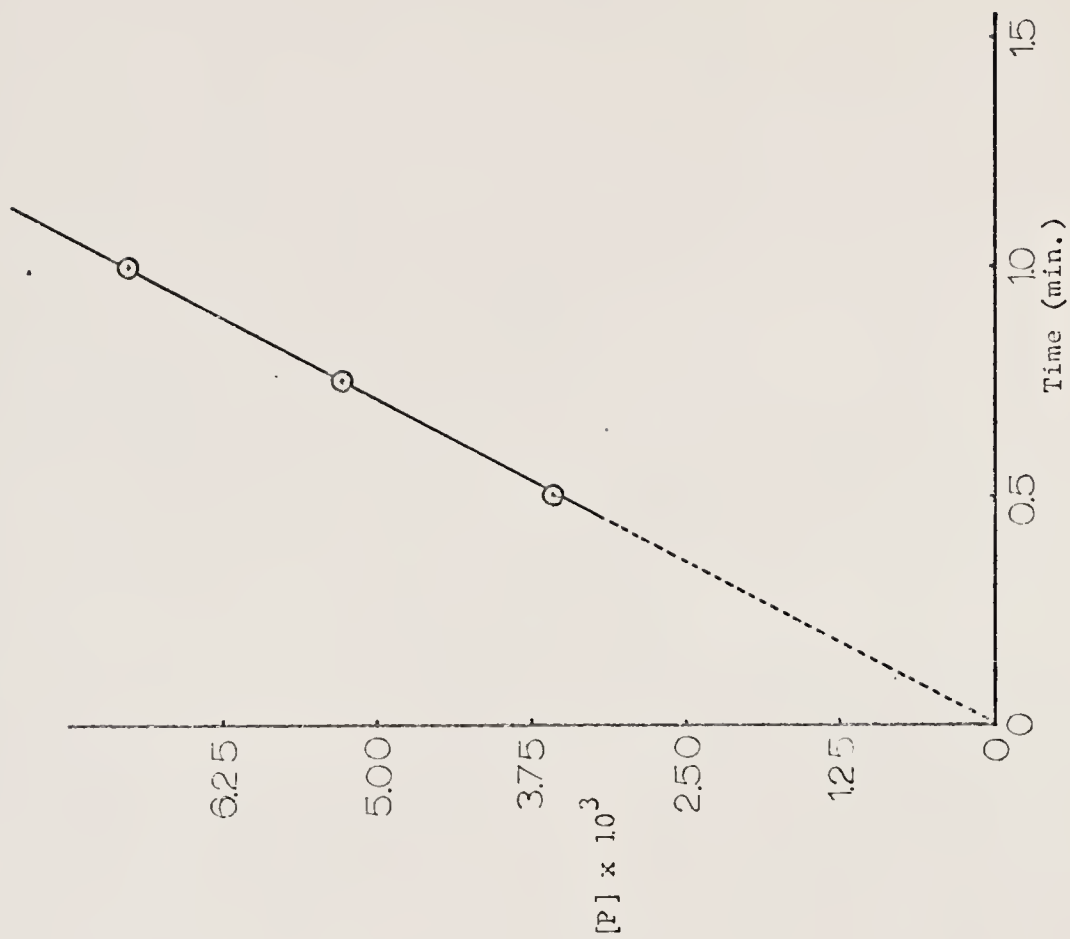
Figure 16

Kinetics of the Anionic Polymerization of Meta-bromo-β-nitrostyrene
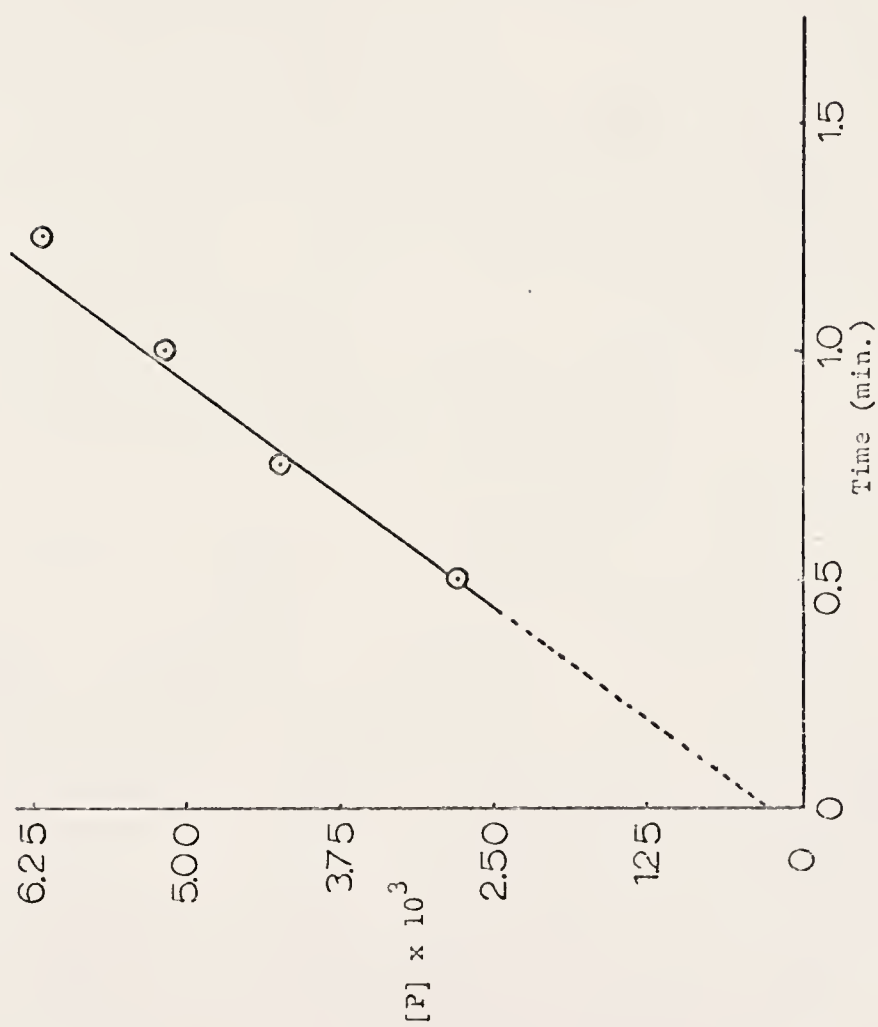
Figure 17

Kinetics of the Anionic Polymerization of Para-bromo-β-nitrostyrene
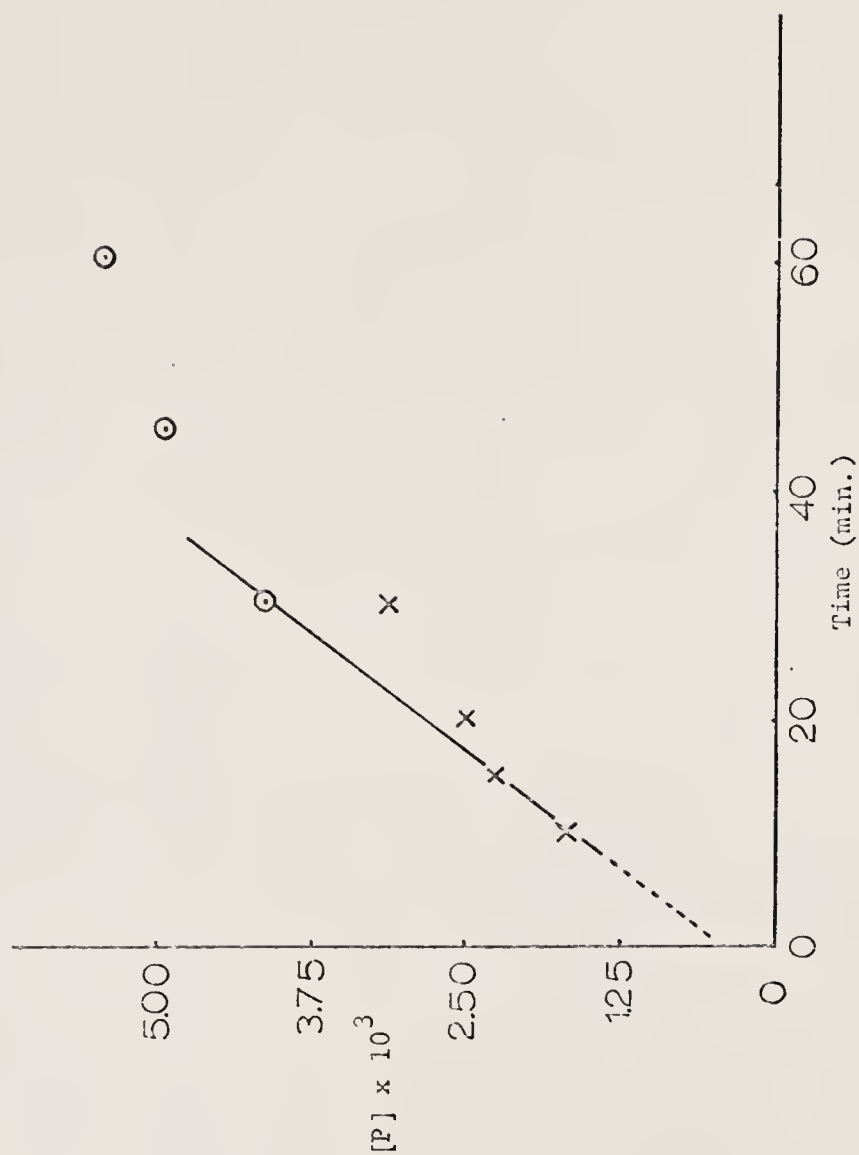
Figure 18

Kinetics of the Anionic Polymerization of Meta,β-dinitrostyrene

TABLE 10

Propagation Rate Constants ($k_p$)

| Substituent | $k_p$ (1. mole$^{-1}$ sec.$^{-1}$) | $k_p/k_o$ |
|---|---|---|
| para-methoxy | 0.38 | 0.42 |
| meta-methyl | 0.57 | 0.63 |
| para-methyl | 0.63 | 0.71 |
| -H | 0.90 | 1.0 |
| para-fluoro | 1.1 | 1.2 |
| meta-methoxy | 1.3 | 1.4 |
| para-chloro | 0.73 | 0.82 |
| para-bromo | 1.4 | 1.6 |
| meta-bromo | 1.8 | 2.0 |
| meta-nitro | 2.2 | 2.5 |

The fact that polymer yield has been shown to be directly proportional
to initiator concentrations (see Figure 19, next page) supports the
assumption that the reactivity of all carbanions is essentially equal.
If there were significant quantities of both tight ion-pairs and the
more reactive solvent-separated ion-pairs, then one would expect a
dilution effect to result in an increased observed rate of polymeriza-
tion as has been observed in the anionically initiated polymerization
of styrene in THF by Szwarc.[65] This would be manifested by a decrease
of the slope of the percent conversion versus initiator concentration
plot. It should be noted that, in this work, this was only tested over
a fairly small range of concentrations (5-fold dilution).

7. The rate of polymerization equals the rate of disappearance
of monomer.-- There were no indications during this study that any side
reactions occured. In view of the fact that possible base catalyzed
Michael addition of ethanol to β-nitrostyrene is merely an extreme of
chain transfer, this possibility need not be considered further in view
of the molecular weight distribution data.

The Hammett plot of the kinetic data (see Figure 20, page 91
showed a surprising resemblance to a similar plot of the data of Kanlet
and Glover,[19] Figure 21, page 92 . This fact alone illustrates the
mechanistic similarity between the base catalyzed Michael addition reac-
tion and the anionic polymerization of α,β-unsaturated compounds. The
fact that both plots definitely show and unusual trend is certainly
reinforcing that an unusual effect is being observed and not merely
experimental error.

Non-straight Hammett plots have been obtained before from many
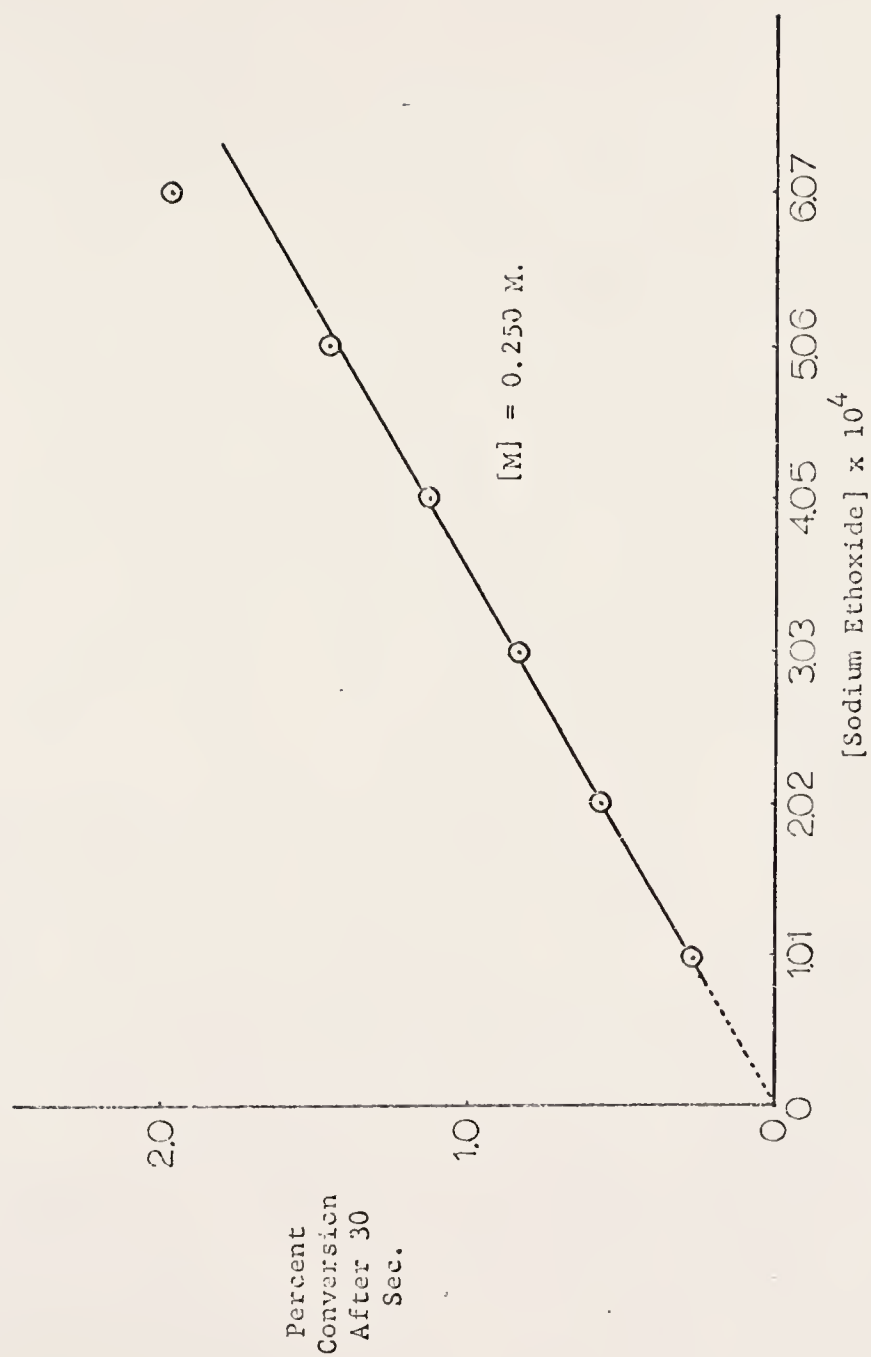organic reactions. However, these have usually been explained on the

Figure 19

Effect of Changes in the Concentration of Initiator on the rate of Anionic Polymer-
ization of β-nitrostyrene

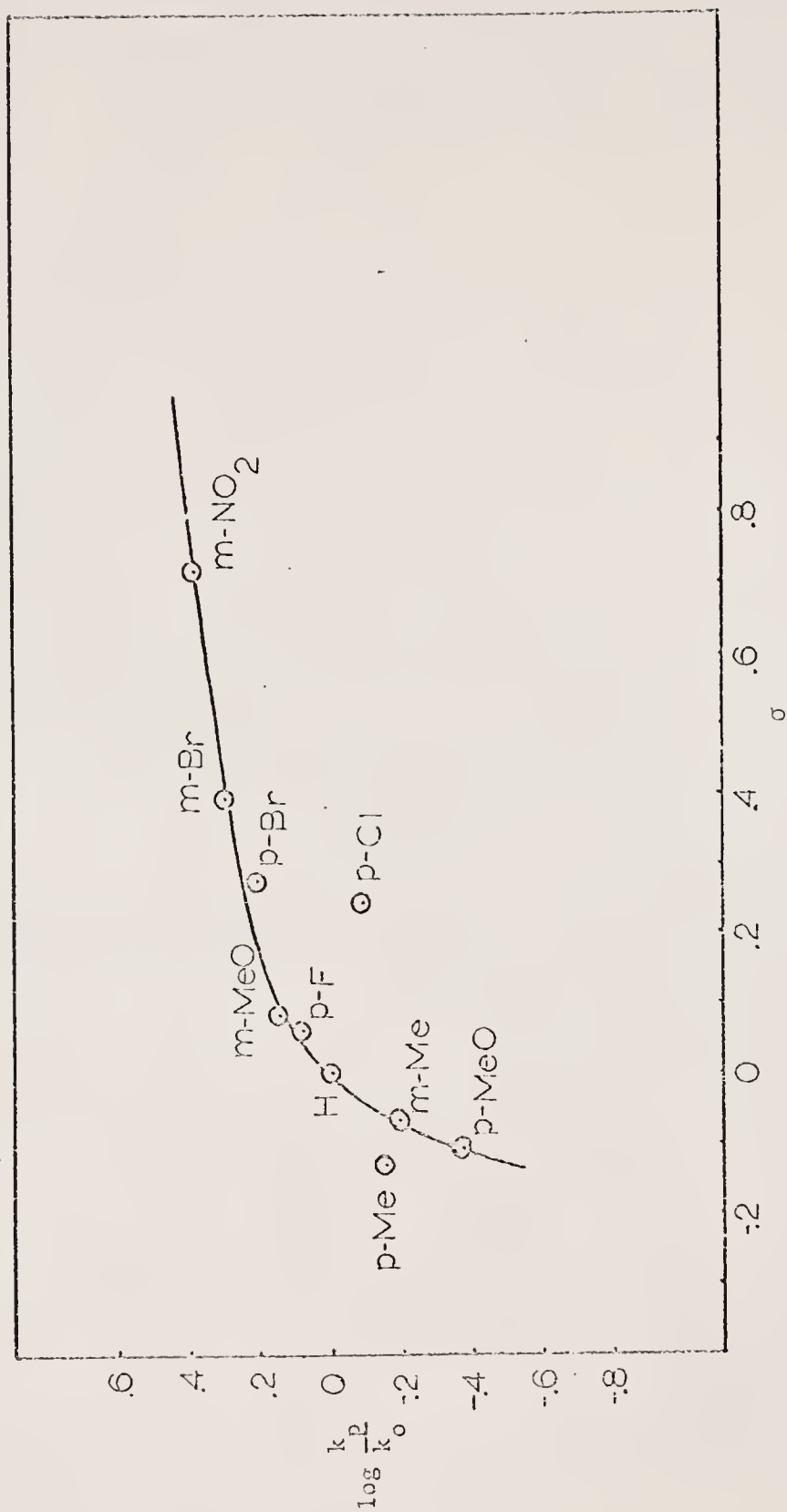Figure 20

Correlation of the Relative Rates of Anionic Polymerization of β-nitrostyrenes with σ
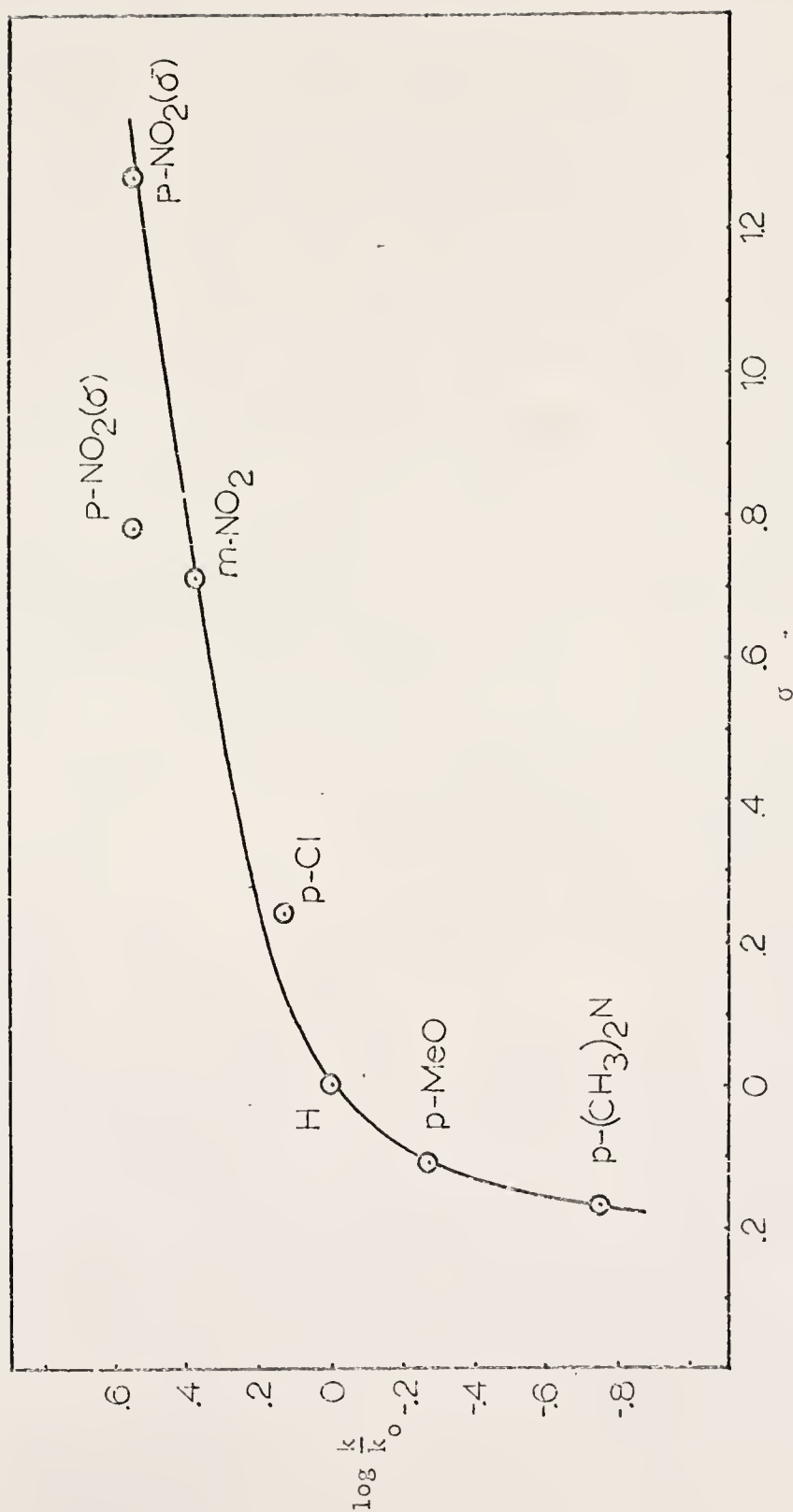
Figure 21

Correlation of the Data of Kamlet and Glover for the Relative Rates of Michael
Addition of Barbituric acid to β-nitrostyrenes with σ

basis of resonance stabilization by conjugated electron withdrawing groups in the case of reactions involving developing negative charge in the rate-determining step and conjugated electron donating groups in the case of reactions involving developing positive charge. Such contributions can usually be corrected for by using $\sigma^-$ and $\sigma^+$ constants, respectively.

One notable exception is the solvolysis of benzyl tosylates in 76.6 mole percent aqueous acetone reported by Kochi and Hammond.[66] Brown later plotted their data against his $\sigma^+$ constants.[37] However, he still observed two distinct slopes. Brown suggested that this was not due to a breakdown in the $\sigma^+$ treatment but rather due to an abrupt change of mechanism from $S_n2$ to $S_n1$ as the electron donating ability of the substituents increased.

It would appear plausible that the distinct change of slope observed in the work of Kamlet and Glover[19] as well as in this work could also be due to a change of mechanism. The commonly accepted mechanism of anionic polymerization of β-nitrostyrene involves attack of the propagating carbanion on the α-carbon of the nitrovinyl moeity of a monomer. This mode of attack has been substantiated by Kamlet[18] for the analogous attack of barbiturate anion on para-dimethylamino, para-chloro, and para-methoxy-β-nitrostyrenes by oxidative degradation of the resulting Michael addition product.

On the other hand, the spectroscopic study of the initiation reaction between sodium ethoxide and meta and para-β-dinitrostyrene indicates that the mechanism of reaction involves the development of a highly conjugated carbanion. Such a species could result from ethoxide attack on the β-carbon of the nitrovinyl moeity. Since the visible

region absorptions of these species persisted during polymerizations of these compounds, the same mechanism of attack was thought to be occurring during propagation. This observation was in agreement with such a change of mechanism.

Furthermore, it was noted that the Hammett plot of the data of Kamlet and Glover[19] (Figure 21, page 92 ) for para-nitro, meta-nitro, para-chloro, and unsubstituted β-nitrostyrene gave a straight line ($\rho = 0.22$) if one used the $\sigma^-$ constant for the para-nitro compound rather than the $\sigma$ constant. Use of the $\sigma$ constant gives a point substantially above the line defined by the other compounds. This also seemed to indicate that the polymerization of these monomers involved a carbanion which was conjugated to the aromatic ring.

If such a change of mechanism were indeed occurring, then this would have been the first reported instance of such a change having been observed in a polymerization reaction. A closer look at the data of Kamlet[18] revealed a discrepancy, however. In that particular paper, he described the reaction of substituted β-nitrostyrenes with barbituric acid and proved the structure of the products by oxidative degradation. Attack of the barbiturate anion on the α-carbon leads to a product which yields the corresponding substituted succinic acid upon oxidative degradation.
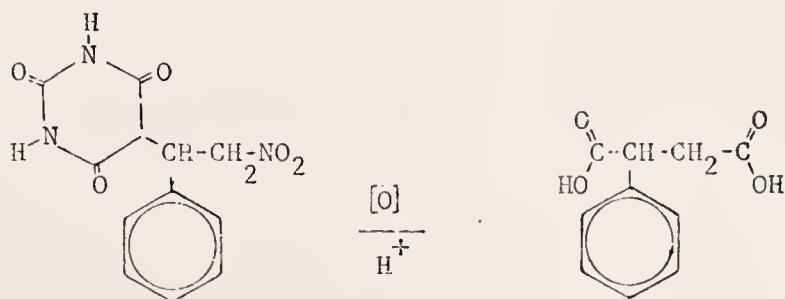
The reaction product with para-chloro-β-nitrostyrene yielded para-chloro-phenylsuccinic acid indicating that barbiturate anion attacks the α-carbon rather than the β-carbon. Attack on the β-carbon would yield a product which would not give succinic acid upon degradation.

To check the significance of this discrepancy, it was decided that the mechanism of attack of a carbanion on meta and para,β-dinitro-styrene should be examined closer. For this reason the reactions between the sodium salt of diethyl malonic ester and meta and para,β-dinitro-styrenes were carried out and the products were degraded with refluxing concentrated hydrochloric acid.

This procedure had already been shown to yield phenylsuccinic acid when applied to β-nitrostyrene.[62] Here it should also yield aromatic-substituted succinic acid if no change of mechanism is occurring. A succinic acid could not be obtained if a change of mechanism is occurring, however. Meta and para-nitrophenyl-succinic acids were obtained in high yields indicating that no change of mechanism was occurring. It should also be noted that the bright red and green colors which resulted from the reaction of sodium ethoxide with para and meta,β-di-nitrostyrene were not observed when sodio-malonic ester was reacted with the monomers.

It would appear that the more nucleophilic less selective sodium ethoxide may attack a nitro-substituted β-nitrostyrene in more than one position whereas the more selective malonate ester carbanion reacts by the most energetically favorable route. The more reactive sodium ethoxide may attack the nitrated β-nitrostyrene either on the β-carbon to form species A or B or on the aromatic ring to form species
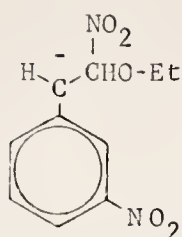
A
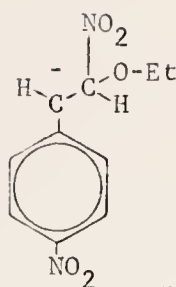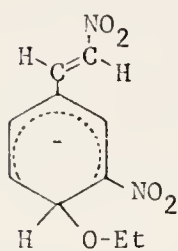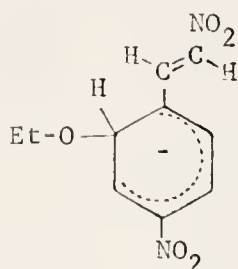


B

C or D.  Nucleophilic attack on the aromatic ring could also occur



C



D

ortho to the β-nitrovinyl group.  In view of the fact that the meta,β-dinitrostyrene-sodium ethoxide adduct absorbed at higher wavelength (657 mμ) in the visible region than the para isomer (539 mμ), the latter mechanism appears more favorable.  It is also possible that species C and D may be much less reactive toward monomer thus explaining the low yields of polymer obtained.

Species C and D are analogous to Meisenheimer complexes such as species E which has been studied in detail by Bernasconi.[67]



E
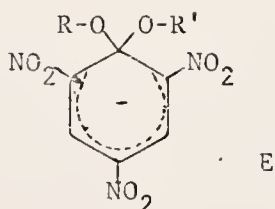
The meta and para,β-dinitrostyrenes are similar to the dinitrobenzenes.
Certain nucleophiles have been found to form Meisenheimer complexes
with meta-dinitrobenzene. Bunnett and Bernasconi[68] have examined the
reaction of piperidine with meta-dinitrobenzene and shown that the
resultant species F absorbs at $\lambda_{max.}$ = 450 mμ. This species is similar



F
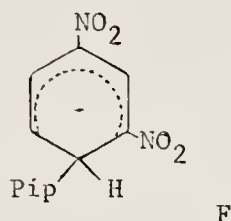
in structure to species C although the nitrostyryl species would be
expected to absorb at longer wavelength.

The cause for the aberrant Hammett behavior observed in this
work as well as the work of Kamlet and Glover[19] is not obvious. It is
obvious that an electron donating substituent in the para position will
increase the electron density in the nitrovinyl group which serves as
an "electron sink". If in the transition state of the propagation step,
the $\alpha$-carbon of the nitrostyryl group is primarily $sp^2$ hybridized, thus
facilitating resonance, then one might expect a type of rate-decreasing
effect due to resonance contribution.

On the other hand, if conjugation between the electron-donating
substituent and the nitro group is lost in the transition state, then
the loss of resonance energy may account for the observed effect.

As previously mentioned, Brown's[37] $\sigma^+$ constants have served to
correct for resonance contributions by electron-donating substituents

in reactions involving the development of conjugated positive charge

in the rate-determining step. In such reactions, e.g., the cationic

polymerization of substituted styrenes as reported by Overberger,[35] the

resonance contributions lead to faster rates of reaction than predicted

by $\sigma$ constants. Since the slope of the Hammett plot is <u>negative</u> in

such reactions, use of the more negative $\sigma^+$ values leads to a better

fit.

In the case of this reaction (whose slope is <u>positive</u>) the

rate-<u>decreasing</u> effects of electron-donating para-substituents would

also be corrected for by using more negative $\sigma$ constants, e.g., Brown's[37]

$\sigma^+$ constants.

The use of Brown's[37] $\sigma^+$ constants gave extremely good correla-

tion both when applied to the data of Kamlet and Glover[19] (Figure 22,

page 99) and this work (Figure 23, page 100). To the best of our

knowledge, this is the first time $\sigma^+$ constants have been found to give

good correlation for a reaction involving the rate-determining attack

of a carbanion.

It would appear that this may also apply to similar reactions

of other compounds such as cinnamonitriles, cinnamic esters, benzal

malonates, and other compounds whose electronic structure is similar

and whose expected mode of reaction with attacking nucleophiles would

be the same.

C.  <u>The Mechanism of Termination in the Anionic Polymerization of Meta
and Para,β-dinitrostyrene</u>

Drueke's observation that the more reactive meta and para,β-

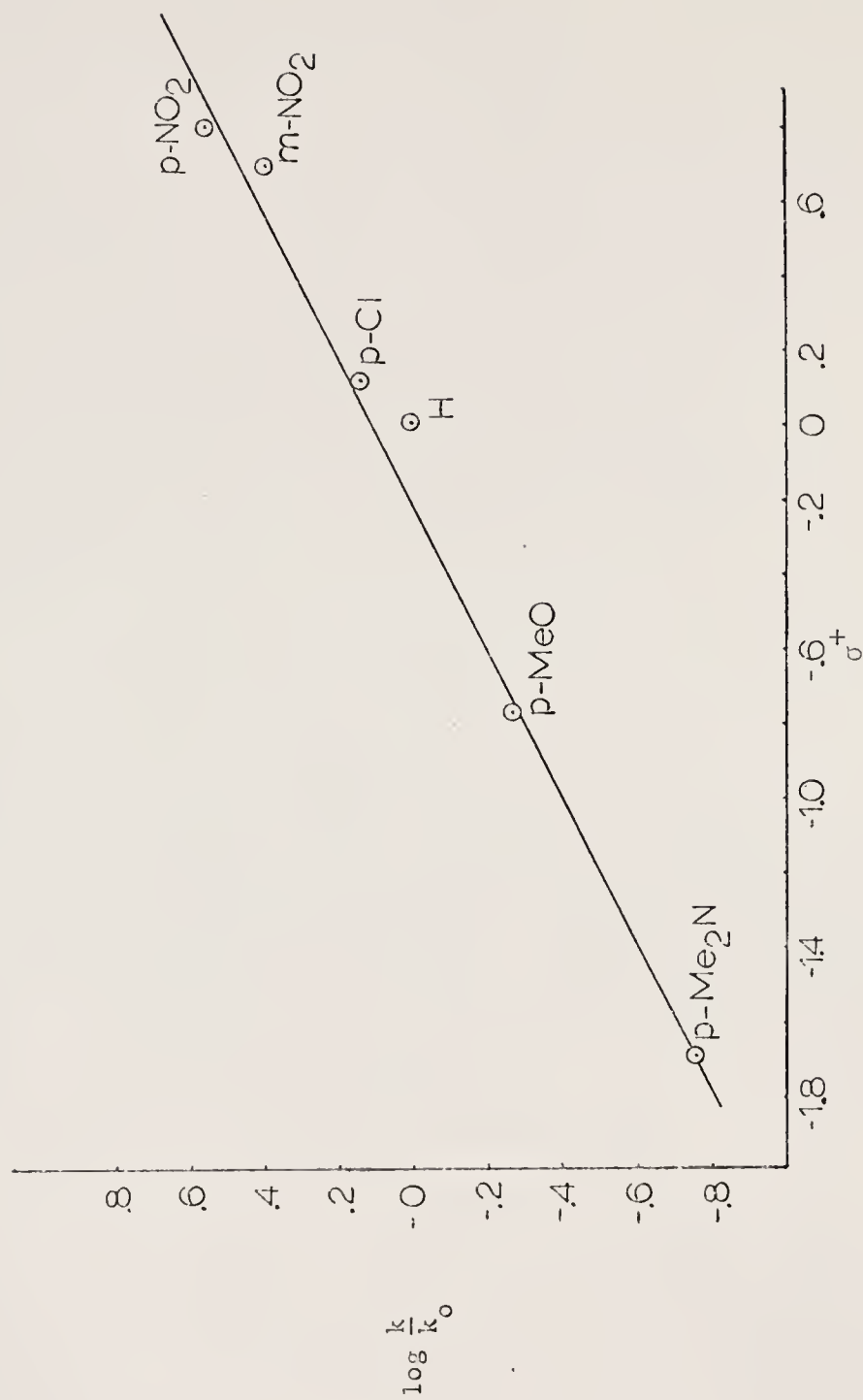dinitrostyrenes gave significantly lower yields upon polymerization

Figure 22

Correlation of the Data of Kamlet and Glover for the Relative Rates of the Michael
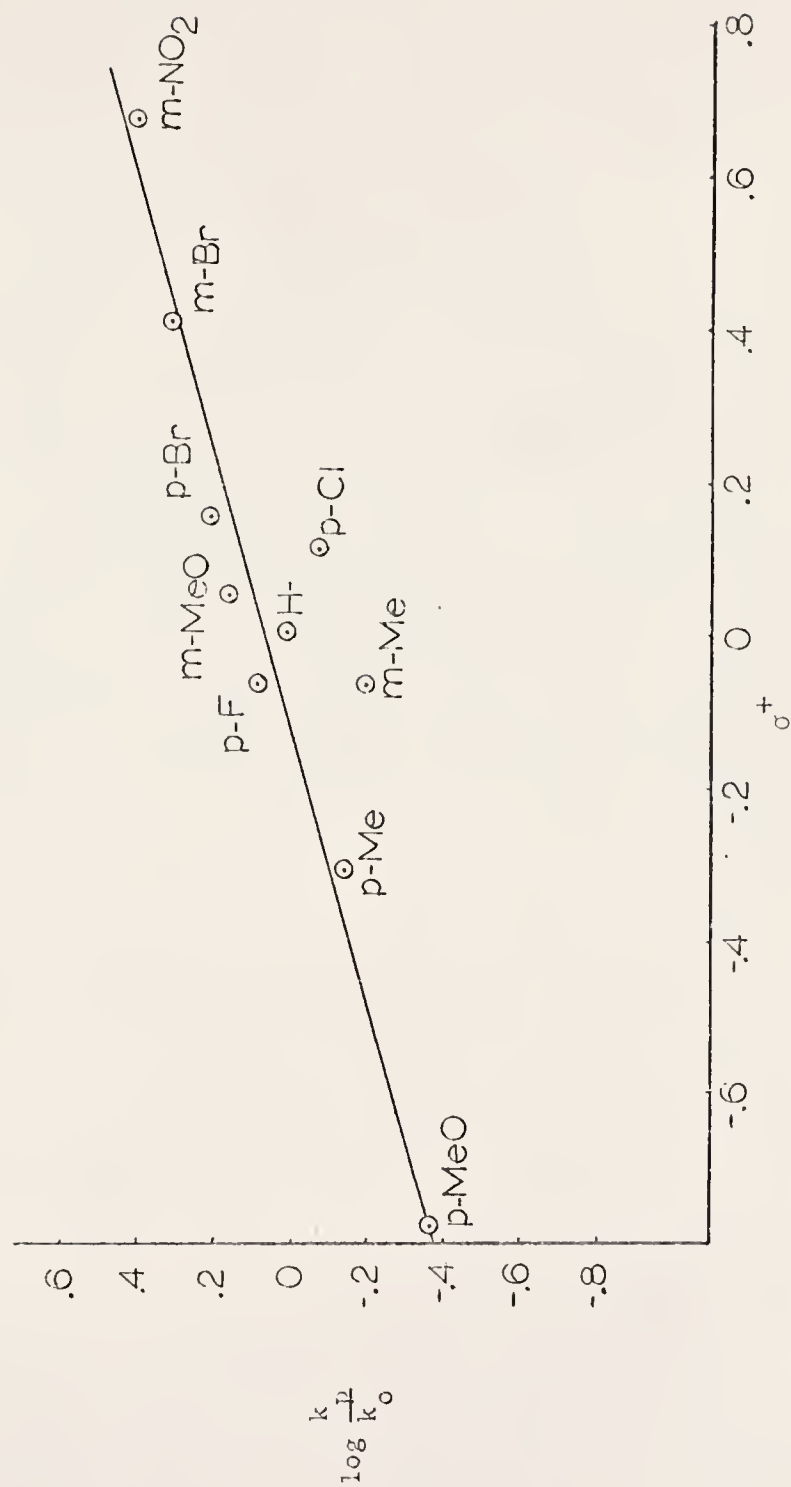Addition of Barbituric Acid to $\beta$-nitrostyrenes with $\sigma^+$

Figure 23

Correlation of the Relative Rates of Anionic Polymerization of $\beta$-nitrostyrenes with $\sigma^+$

than less reactive monomers has been well substantiated in this study.
While meta and para-methoxy-β-nitrostyrenes gave 95.8 and 94.8 percent
conversions, respectively, when polymerized with three mole percent
initiator; meta and para-β-dinitrostyrenes gave only 22 and 5.2 percent
conversions, respectively, when polymerized with five mole percent
initiators. These relatively low yields suggest that either the molec-
ular weights were extremely low or a significant amount of polymer was
not isolated. The nmr spectra of the recovered monomers included
unidentifiable weak but broad peaks which were probably attributable
to soluble polymeric material.

However, the low yields are probably primarily due to a type
of auto-termination brought about by the relatively high acidity of the
polymer. The data obtained supports the hypothesis that a propagating
carbanion may either continue to propagate or, in a "back biting" fashion,
abstract a proton to form a new and impotent carbanion of the polymer
chain.
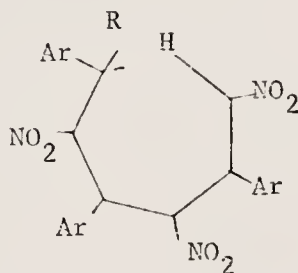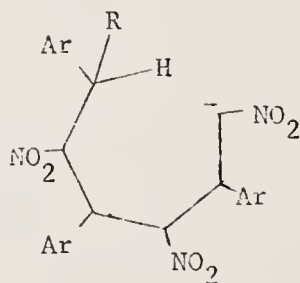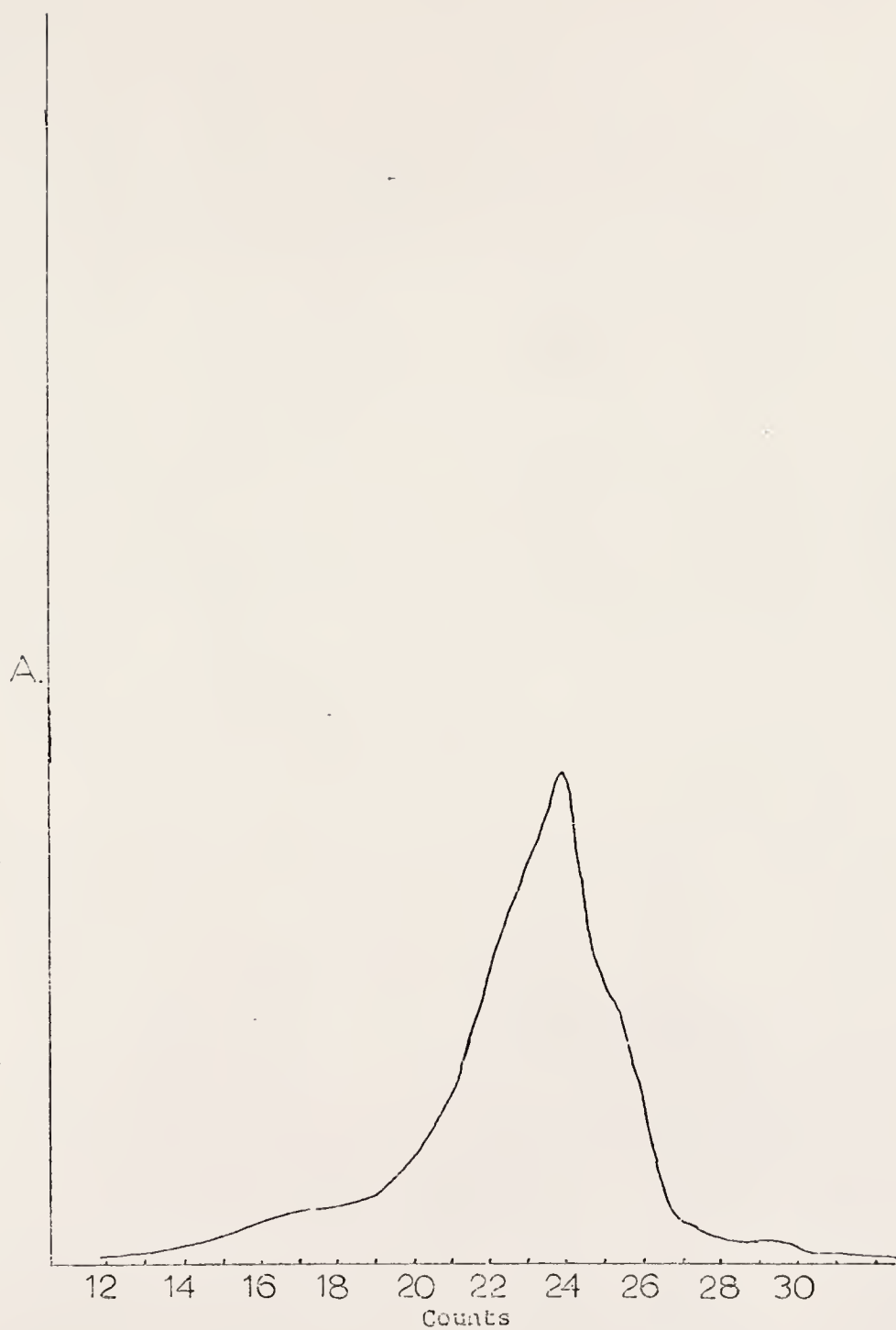
R = polymer chain

Ar = aromatic ring

Figure 24
The Molecular Weight Distribution Curve of Poly-meta-
β-dinitrostyrene

This process could occur intermolecularly as well. The reluctance of this new species to graft polymerize could be the result either of steric considerations or its weaker nucleophilicity. The fact that solutions of the polymers and sodium ethoxide did not initiate any detectable polymerizations when mixed with other substituted β-nitrostyrenes supported this hypothesis.

This auto-termination also accounted for the unusually broad molecular weight distribution curve for poly-meta,β-dinitrostyrene (Figure 24, page 102) as well as the large ratio of $\overline{M}_w/\overline{M}_n$ for that polymer (7.33).

## D. The Ortho-effect

Drueke's observation of a marked ortho effect as manifested by substantially lower yields of polymer was also well substantiated in this study. Ortho-fluoro-β-nitrostyrene gave a 26.3 percent conversion when polymerized with three mole percent sodium ethoxide compared with 75.2 and 90.5 percent conversions, respectively, for the meta and para isomers under identical conditions.

No other ortho-substituted β-nitrostyrenes (all with larger substituents than fluoro) gave more than 1.77 percent conversion to ethanol insoluble product. It should be noted that the fluoro substituent was the smallest substituent used in this study.

The kinetic study revealed that the rate of polymerization of the ortho-fluoro isomer is quite constant at low conversion. The fact that the kinetic plot (Figure 25, page 104 ) intersected the 0,0 coordinate supports the hypothesis that initiation of the polymerization is relatively fast and that the observed rate of polymerization represents
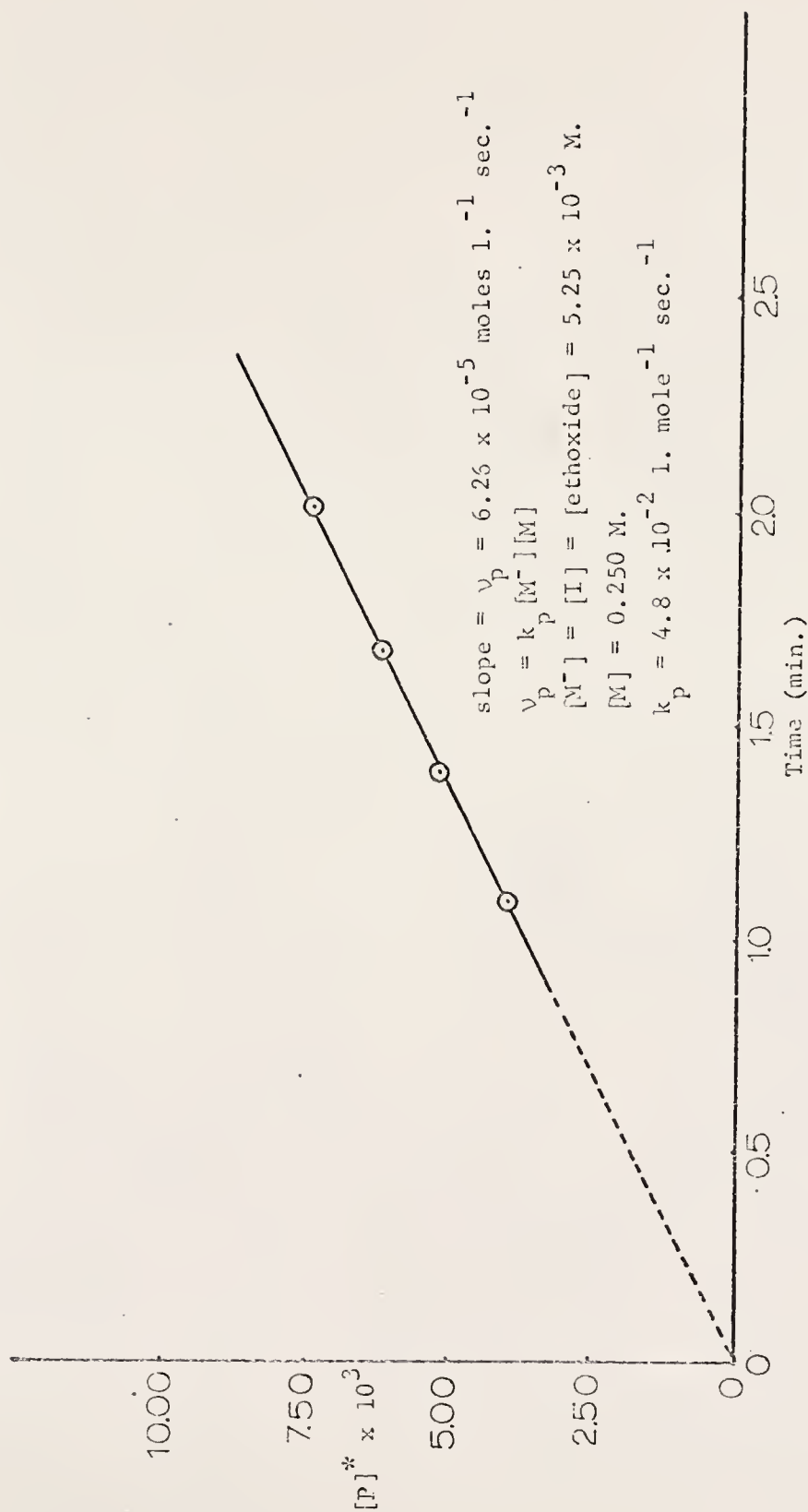
slope $= \nu_p = 6.25 \times 10^{-5}$ moles l.$^{-1}$ sec.$^{-1}$

$\nu_p = k_p [N^-][M]$

$[N^-] = [I] = [ethoxide] = 5.25 \times 10^{-3}$ M.

$[M] = 0.250$ M.

$k_p = 4.8 \times 10^{-2}$ l. mole$^{-1}$ sec.$^{-1}$

Time (min.)

$[P]^* \times 10^3$

Figure 25

Kinetics of the Anionic Polymerization of Ortho-fluoro-β-nitrostyrene

*[P] is polymer yield expressed in terms of monomer units (moles liter$^{-1}$) converted to polymer

the rate of propagation. The value obtained for the propagation rate
constant ($k_p$ = 4.8 x $10^{-2}$ 1. mole$^{-1}$ sec.$^{-1}$) quantitatively illustrates
the magnitude of the ortho effect; $k_p$(para)/$k_p$(ortho) = 22.

The experiments which involved reaction of ortho-fluoro, chloro,
bromo, methoxy, and (2-vinyloxy)ethoxy-β-nitrostyrenes with excess sodium
ethoxide (monitored by nmr) conclusively showed that the presence of
relatively large ortho-substituents does not prevent nucleophilic attack
by the ethoxide (initiator). The nmr spectra (Figures 26-30 on the
following pages) indicated that all five compounds reacted quantita-
tively with an excess of sodium ethoxide within 30 seconds. No quan-
titative determination of the rate of initiation was made. Qualitatively,
however, it appears that there is little steric effect exerted on the
process of initiation. Therefore the "ortho-effect" is probably the
result of inhibition of propagation. This could be due to the fact
that the initial nitrovinyl group exists in a conformation which keeps
it nearly coplanar with the aromatic ring so as to preserve conjugation.
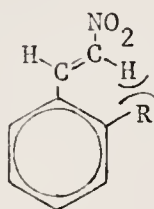
This conformation might result in the existence of a form of
Pitzer strain between the α-hydrogen of the nitrovinyl group and larger
ortho-substituents. Thus, it can be seen that initiation, which should
occur from a position perpendicular to the plane of the coplanar ring
and nitrovinyl group, would result in the relief of this strain. How
the substituent exerts an inhibitive effect on the reaction of the
carbanion on the β-carbon is not presently understood.

Figure 26
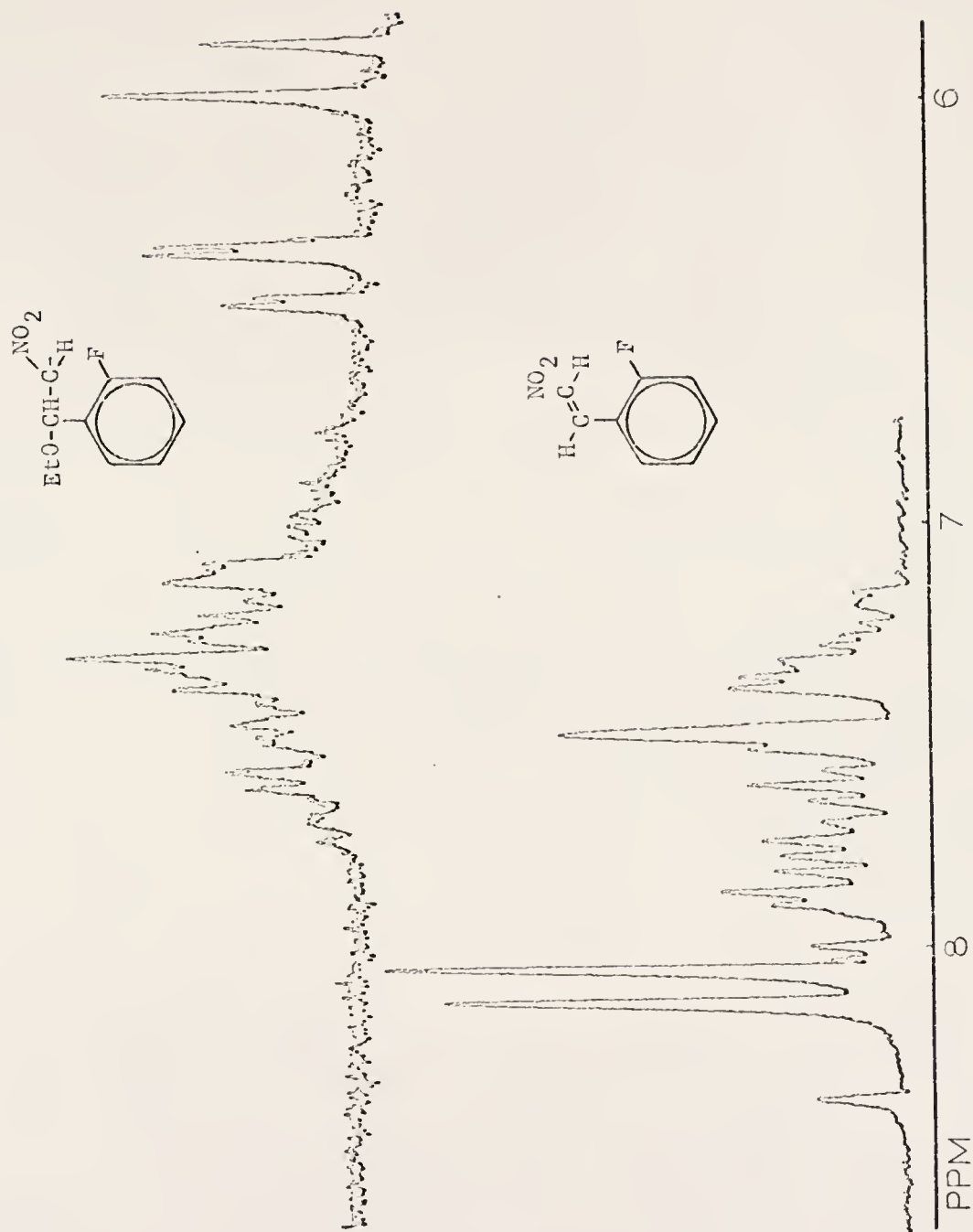
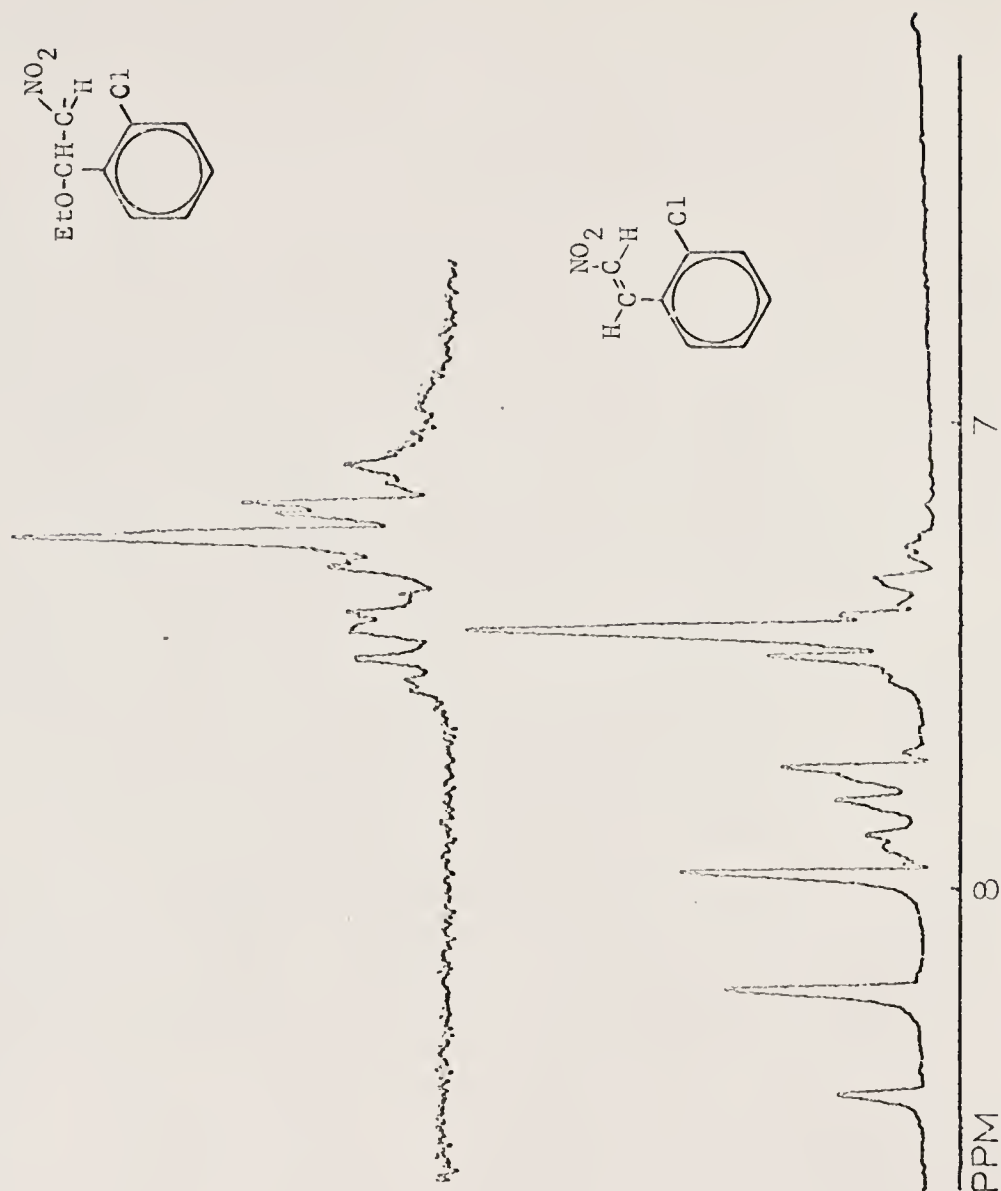The Reactivity of Ortho-fluoro-β-nitrostyrene with Sodium Ethoxide

Figure 27

The Reactivity of Ortho-chloro-β-nitrostyrene with Excess Sodium Ethoxide

Figure 28
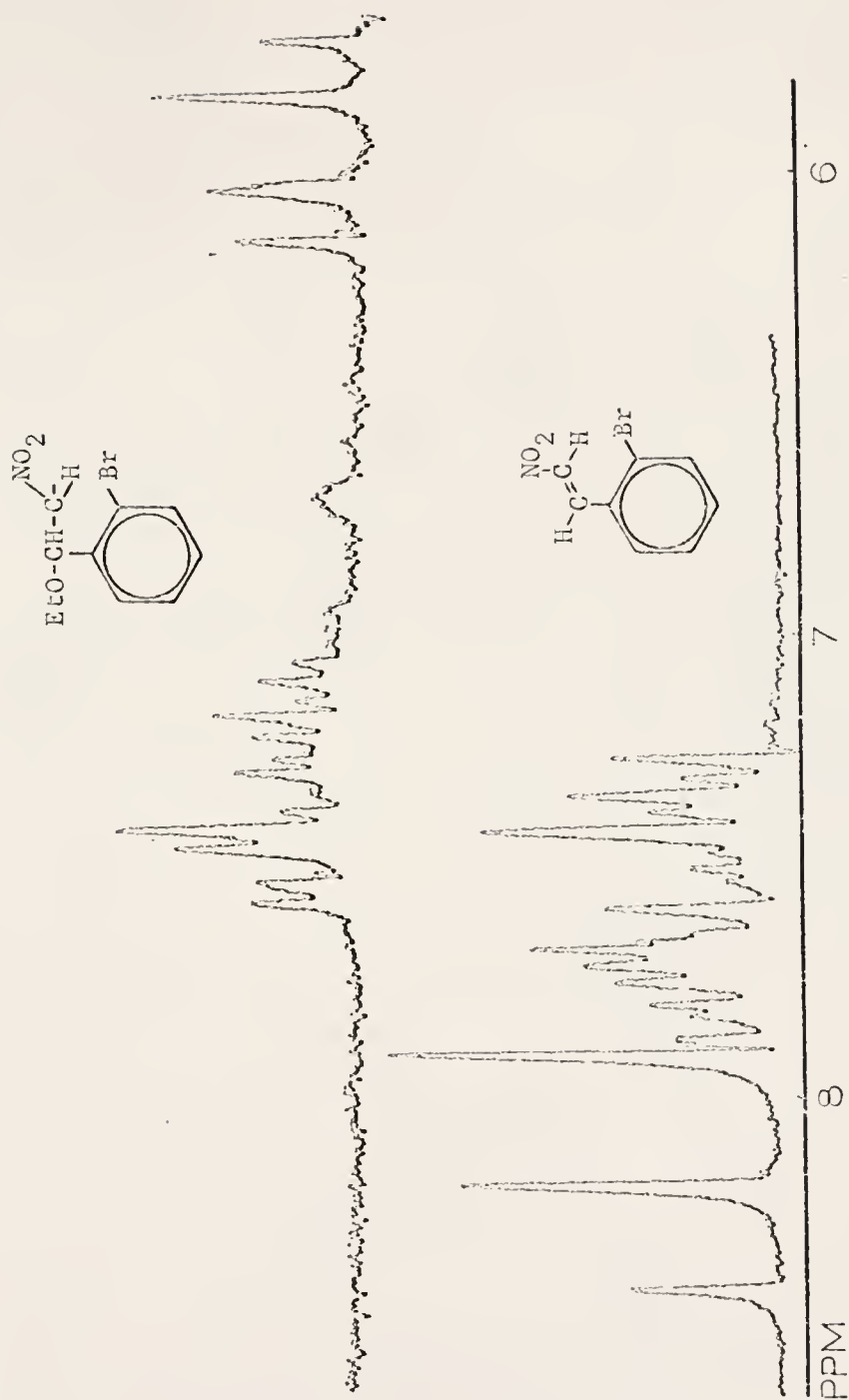
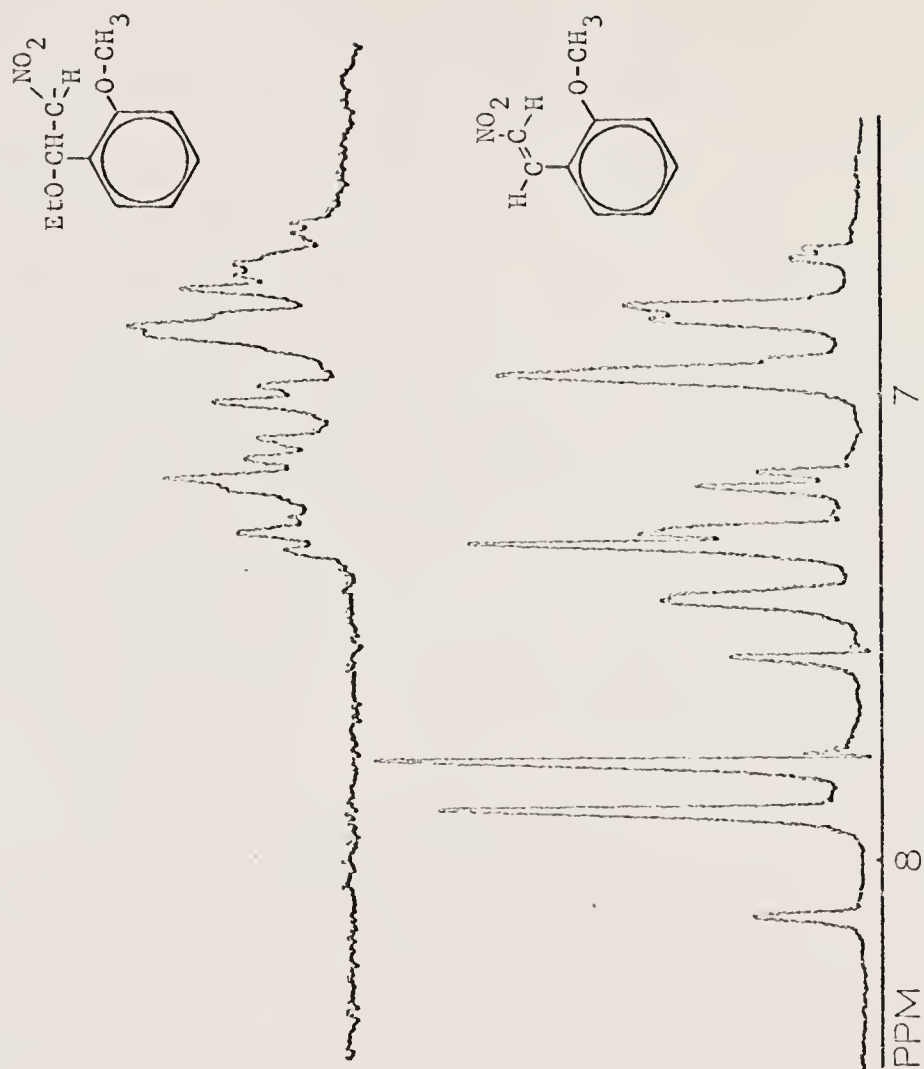The Reactivity of Ortho-bromo-β-nitrostyrene with Excess Sodium Ethoxide

Figure 29

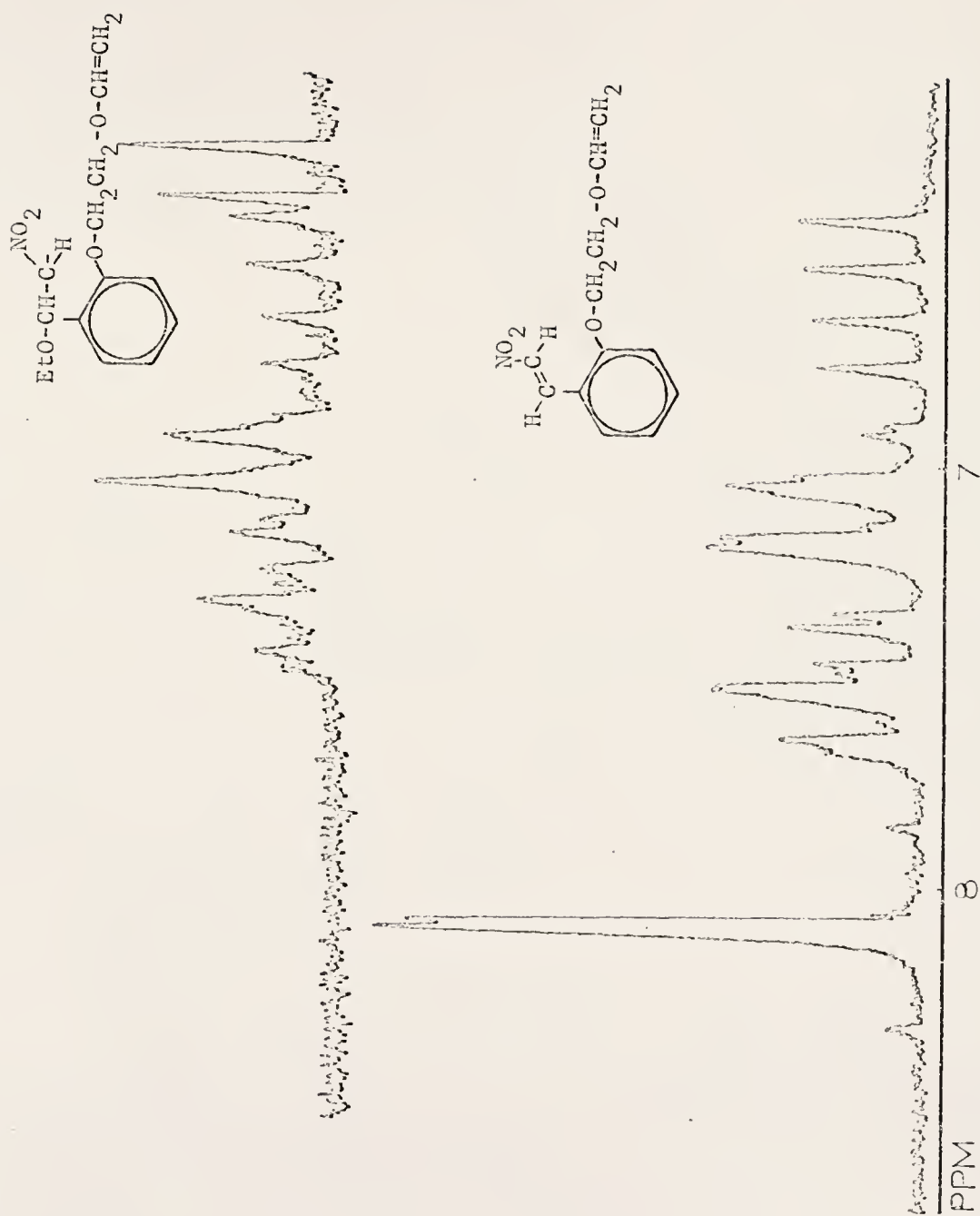The Reactivity of Ortho-methoxy- β-nitrostyrene with Excess Sodium Ethoxide

Figure 30

The Reactivity of Ortho(2-vinyloxy)ethoxy-β-nitrostyrene with Excess Sodium Ethoxide

The hypothesis that attack on the α-carbon of the nitrovinyl group is not sterically inhibited would appear to be well supported by the previously mentioned work of Worrall[20,21,22,23] who reacted various amines with ortho-substituted β-nitrostyrenes and obtained 1:1 adducts. However, it should be noted that the recent work of Lough and Currie,[69] who conducted kinetic studies of the reaction of butyl amine with various β-nitrostyrenes, indicates that the rate determining step of this reaction is not a simple nucleophilic attack. They obtained a negative value of ρ from their Hammett treatment which would indicate that the transition state of the rate determining step involves some degree of proton transfer to the substrate. Those workers hypothesized a transition state involving a six-centered ring. It is obvious, however, that
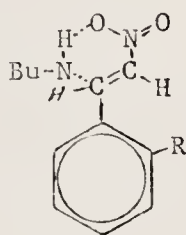


the reaction does not involve a rate-determining attack on the β-carbon and no ortho-effect is observed.

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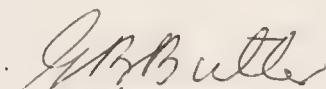47. P. J. Flory, J. Am. Chem. Soc., 65, 372 (1943).

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James Wesley Schwietert was born July 2, 1944, in Medford, Oregon, and raised on a small cattle ranch near Phoenix, Oregon. In June, 1962, he was graduated from Phoenix High School. In June, 1966, he was awarded the degree Bachelor of Science, cum laude, with a major in chemistry and a minor in zoology from Southern Oregon College. In September, 1966, he enrolled in the Graduate School of the University of Florida as the recipient of a National Science Foundation Science Development Assistantship. He was also awarded an Interim Instructorship for one year by the Department of Chemistry. He has pursued his work toward the degree of Doctor of Philosophy since entering graduate school.

James Wesley Schwietert is married to the former Patricia Rose English. He is a member of Alpha Chi Sigma and the American Chemical Society.
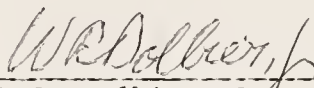
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Assistant Professor of Chemistry

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Professor of Chemistry